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SALINE GROUNDWATERS PRODUCED WITH OIL AND GAS

A. Gene Collins

Bureau of Mines

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7. Author(s)
A. Gene Collins

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~~Bartlesville, Okla. 74003~~

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16. Abstract

More than 60,000 saline water analyses were collected by the U.S. Bureau of Mines for entry into an automatic data processing system. Screening of the data eliminated 30,000 analyses; 20,000 were entered into STORET, the data processing system formulated by the Environmental Protection Agency.

The water analyses are used in studies related to identifying the source of a brine, classification of groundwater for use in geochemistry, plotting local and regional salinity maps, determining sources of pollution of freshwater and land by brines, and studies of the use of saline water for desalination to produce freshwater and valuable minerals. Examples of each of these studies are given ~~in this report.~~

Irresponsible control of brines can seriously pollute freshwater and land. The analyses now in STORET should be wisely used in pollution prevention programs. Additional analyses should be entered into STORET to aid groundwater and land pollution prevention programs.

The most important factors are the potentials that exist for using the data in studies related to pollution abatement and exploration for minerals. ~~(Credit: USBM)~~ (EPA)

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April 1974

SALINE GROUNDWATERS PRODUCED WITH OIL AND GAS

By

A. Gene Collins
U.S. Department of the Interior
Bureau of Mines
Bartlesville Energy Research Center
Bartlesville, Oklahoma 74003

Project 16060 EQQ
Program Element 1BA024

Project Officer

Jack W. Keeley
Robert S. Kerr Environmental Research Laboratory
U.S. Environmental Protection Agency
Ada, Oklahoma 74820

Prepared for

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ABSTRACT

More than 60,000 saline water analyses were collected by the U.S. Bureau of Mines for entry into an automatic data processing system. Screening of the data eliminated 30,000 analyses; 20,000 were entered into STORET, the data processing system formulated by the Environmental Protection Agency; and 10,000 additional analyses could be entered with additional funding.

The water analyses are used in studies related to identifying the source of a brine, classification of groundwater for use in geochemistry, plotting local and regional salinity maps, determining sources of pollution of freshwater and land by brines, and studies of the use of saline water for desalination to produce freshwater and valuable minerals. Examples of each of these studies are given in this report.

Irresponsible control of brines can seriously pollute fresh water and land. The analyses now in STORET should be wisely used in pollution prevention programs. Additional analyses should be entered into STORET to aid groundwater and land pollution prevention programs.

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SECTION I

CONCLUSIONS

The 20,000 saline water analyses that were entered into STORET will be useful in preventing pollution of freshwater and land by brines. These analyses can be used in identifying the source of a saline water that is polluting a freshwater. Salinity maps of local or regional areas can be plotted with the analyses and used to determine potential waste disposal zones and potential pollution areas, such as possible brine intrusion horizons. The maps also will be useful in locating saline waters that can be desalinated for the production of freshwater and/or valuable minerals. Additional saline water analyses should be added to STORET to aid these study areas.

SECTION II

RECOMMENDATIONS

It is recommended that EPA add additional saline water analyses to STORET, especially analyses that include minor and trace constituent data in addition to the macroconstituents. Local and regional maps should be prepared from the saline water analyses and used in groundwater, surface water, and land pollution studies. Once a groundwater is polluted by a brine it can take several hundred years before the polluted area is once again useful as a freshwater source. Therefore, stringent regulations should be formulated and enforced. A saline groundwater monitoring program should be established.

SECTION III

INTRODUCTION

GENERAL

In the early days of the oil industry, oilfield brines were allowed to flow by natural drainage into streams until it was noted that some of the once-good fishing streams contained less fish, that fur-bearing animals had disappeared in these areas, and dead trees and barren soils now bordered these same streams that once had luxurious vegetation. A few years prior to 1935, litigation pertaining to pollution of freshwater was taking a heavy toll from oil operators. In certain older oil-producing areas, extensive plots of ground still are barren, with no living vegetation. The litigations against oil operators combined with legislation for freshwater protection to force better disposal techniques.

At first, evaporation ponds were employed; however, usually more brine drained into freshwater aquifers than evaporated. Until recently, a widely employed practice for disposal was the dumping of oil brines into freshwater bodies when they existed nearby. This disposal method was practiced along the Gulf of Mexico and in California. Authorities in these areas insisted that oil separation be highly efficient to prevent damage to fish and oyster populations. Recently the state pollution boards have ruled that oilfield brines can no longer be dumped into surface saltwater bodies. In California, excess oilfield waters now are being injected into porous subsurface formations as rapidly as the injection systems can be constructed.

The plains states not only are situated in a hard water belt, but seldom have had an overabundance of usable or surface groundwater. For this reason, State legislatures passed laws for the protection of freshwater supplies, allowing the

return of oilfield brines to subsurface formations and allowing the repressuring or waterflood of oil properties with saltwater. Subsurface brine disposal has since become the common practice. Since the laws were passed to allow subsurface disposal, legislation has forced such disposal and set up tight controls for it. A survey of cost data on subsurface injection in 1968 showed that subsurface disposal costs ranged from 6.6 to 19.8 cents per cubic meter. These figures were based on operating costs plus 5-year amortization.

Costs vary with the amount of treatment necessary before injection, the number of production wells per injection well, and the costs of drilling injection wells or the depth of the injection formation. The depths of disposal wells normally encountered required no injection pressure. The brines normally flow readily into the receiving formations under the gravity head alone.

The annual production of 1.23 billion cubic meters of saline water in association with petroleum in the United States is an expense to oil producers even though some of these waters contain salts yielding valuable elements that might be economically recovered. Elements found in some brines in economic concentrations are magnesium, calcium, potassium, lithium, boron, bromine, and iodine. Many of them are recovered by chemical companies from seawater, salt lakes, and subsurface saline waters.

The recovery of minerals from saline waters dates back to the first time that someone precipitated a compound from a salt solution. Precipitation is the most used separation process employed in separating minerals from seawater or subsurface brines. Research continues on the separation methods which show economic promise in mineral separation from saline waters.

Commonly the waters from different strata differ considerably in their dissolved chemical constituents, making the identification of a water from a particular strata easy. However, in some areas, the concentrations of dissolved constituents in waters

from different strata do not differ significantly, and the identification of such waters is difficult or impossible.

The amount of brine produced with the oil often increases as the amount of oil produced decreases. If this is edge water, nothing can be done about it. If it is bottom water, the well can be plugged back. However, it often is intrusive water from a shallow sand gaining access to the well from a leaky casing or faulty completion, and this can be repaired.

OBJECTIVE

The project objective was to establish an automatic data processing reference system for subsurface saline waters in the STORET format and to show its use in determining the sources of ground water and surface water pollution resulting from oil and gas production and deep well disposal. (STORET is the central computer-oriented U.S. Environmental Protection Agency Water Quality Control System for storing and retrieving water data and water-related data.) In addition, this saline water reference system can be used to plot water analyses diagrams for use in saline water intrusion studies, plot cross-section or contour salinity maps to study large areas of possible pollutants, and to determine areas where desalination to produce freshwater and valuable byproduct minerals might be feasible.

Scope

Brine analyses from most of the oil and gas producing sedimentary basins of the United States were collected from government agencies and oil companies and entered into the STORET system. This report examines the following areas:

1. Saline water analyses stored in STORET.
2. Methods of identifying a water source.
3. Saline water classification.
4. Plotting salinity maps for use in local or regional studies.
5. Pollution of freshwater and land by brines.
6. Use of brines for desalination to produce freshwater and valuable minerals.

SECTION IV

SALINE WATER ANALYSES STORED IN STORET

More than 60,000 saline water analyses were collected from various governmental and industrial sources. The primary method of collection was microfilming of the original documents. The microfilmed data then were restored to their original size with a Xerox microfilm printer. The data were examined to insure that they were usable and complete.

This screening process eliminated about 30,000 analyses because of incomplete sample description, incomplete analyses of the macro constituents (sodium, calcium, magnesium, bicarbonate, chloride, and sulfate), or an obviously poor sample or poor analysis. Funding of the project permitted the entry of 20,000 analyses into STORET. At least 10,000 good additional analyses could be entered into STORET with additional funds. Table 1 shows the number from each oil-producing state.

The STORET saline groundwater data format shows the location in latitude and longitude, the major river basin, the major geologic province, geologic era, geologic system, and geologic formation, together with the depth of the well, date sampled, and the chemical and physical analyses of the sample.

Problems previously encountered with coding were eliminated by the use of standard codes obtained for the parameters that were not previously in the STORET system; the geologic system, series, and formation for a particular sample are coded from data obtained from the Bulletin of Standard Stratigraphic Codes adopted by the American Association of Petroleum Geologists. The use of these codes eliminates duplicity of coding because each formation has a specific alphanumeric listing.

Table 1. NUMBER OF SALINE WATER ANALYSES FROM OIL-PRODUCTIVE STATES ENTERED INTO STORET

State	Number of samples
Alabama	90
Alaska	112
Arizona	15
Arkansas	573
California	109
Colorado	1,032
Illinois	543
Indiana	443
Kansas	2,350
Louisiana	1,695
Michigan	347
Mississippi	320
Montana	1,083
Nebraska	325
New Mexico	388
New York	2
North Dakota	301
Oklahoma	1,769
Pennsylvania	90
South Dakota	73
Texas	2,820
Utah	489
Wyoming	5,000
Total	19,969

Appendix I illustrates the format used for coding of the data that is entered into the STORET system. A retrieval of the data entered into STORET for the State of Texas was completed to determine if the material was properly formated. Appendix II is an example of a retrieval for the same sample illustrated in Appendix I.

SECTION V

METHODS OF IDENTIFYING A WATER SOURCE

Water analyses may be used to identify the source of a water. In the oilfield one of the prime uses of these analyses is to determine the source of extraneous water in an oil well. A leak may develop in the casing or cement, and water analyses are used to identify the water-bearing horizon so that the water zone can be squeeze cemented to prevent water from flooding the oil or gas horizon. With the present emphasis on water pollution prevention, it is very important to locate the source of a polluting brine so that remedial action can be taken.

Comparisons of water-analysis data are tedious and time consuming; therefore, graphical methods are commonly used for positive, rapid identification. A number of systems have been developed, all of which have some merit.[1,2,3,4]

CALCULATING PROBABLE COMPOUNDS

The hypothetical combinations of dissolved constituents found in waters are commonly calculated by combining the positive and negative radicals in the following order:

Cation, positive	Anion, negative
Calcium	Bicarbonate
Magnesium	Sulfate
Sodium	Chloride
Potassium	Nitrate

Calcium is combined with bicarbonate, and if more calcium is available than that consumed by bicarbonate, it is combined with sulfate, chloride, and nitrate until exhausted. Conversely, any excess bicarbonate is combined with magnesium, sodium, and potassium until consumed. Other radicals can and should be added

for most petroleum reservoir waters. These include lithium, strontium, barium, iron, borate, phosphate, bromide, and iodide. They can be grouped in the appropriate column and then in the calculation; as each positive and negative radical is totally combined, the next following radical is combined until both the cations and anions are exhaused. If the analysis is correct, the cations and anions will be present in approximately equivalent amounts.

To calculate the hypothetical combinations, the reacting values of the positive and negative radicals or ions are calculated as follows: Reacting values (R.V.) or equivalents per million (epm) = mg/l, ion x (valence of ion)/(m.w. of ion).

The term (valence of ion)/(m.w. of ion) is called "reaction coefficient" and the positive and negative ions have values as shown in Table 2. Table 3 indicates how the results of a water analysis are converted to reacting values.

Table 2. REACTION COEFFICIENTS

Cation		Anion	
Calcium	0.0499	Bicarbonate	0.0164
Magnesium	0.0823	Sulfate	0.0208
Iron	0.0358	Chloride	0.0282
Sodium	0.0435		

Table 3. REACTING VALUES (R.V.)

Cation, mg/l		R.V.	Anion, mg/l		R.V.
Ca	4,000 x 0.0499 =	199.6	HCO_3	500 x 0.0164 =	8.2
Mg	3,000 x 0.0823 =	246.8	SO_4	200 x 0.0208 =	4.2
Fe	100 x 0.0358 =	3.6	Cl	30,000 x 0.0282 =	846.3
Na	9,400 x 0.0435 =	408.9			
		858.9			858.7

The reacting values are a measure of the cations and anions dissolved in the water. With a reacting value of 199.6, the 4,000 mg/l of calcium in the example shown in Table 3 can combine with all the bicarbonate, all the sulfate, and 187.2 epm of the chloride. Magnesium will combine with 246.8 epm of chloride, iron with 3.6, and sodium with 408.9. Thus the reacting values can be considered to be distributed as shown in Table 4.

Table 4. REACTING VALUE DISTRIBUTION

Ca as calcium bicarbonate	8.2
Ca as calcium sulfate	4.2
Ca as calcium chloride	187.2
Mg as magnesium chloride	246.8
Fe as iron chloride	3.6
Na as sodium chloride	408.9
	858.9

A charge balance should be determined on the brine analysis. This can be done using the equation: $(x - y)/(x + y) \times 100 = \%\ CB$

where x = total positive ions (epm)

y = total negative ions (epm)

CB = charge balance error and it should always be less than 2% for a brine.

DETERMINING A SOUGHT COMPOUND

It is necessary to multiply the reacting value of an anion or a cation by a combination factor to determine a hypothetical compound. This factor is necessary to convert the reported radical into the desired compound. For example, the factor

for converting Ca to $CaCO_3$ is $CaCO_3/Ca$ or 2.50 and the reaction coefficient for Ca is 1/(Ca/2) or 0.0499. Therefore, the combination factor to convert the reacting value for Ca to $CaCO_3$ is 2.50 ÷ 0.0499 = 50.1. Table 5 illustrates some combination factors.

Table 5. COMBINATION FACTORS

Reaction values given	Compound sought	Combination factor
Ca or CO_3	$CaCO_3$	50.1
Ca or SO_4	$CaSO_4$	68.1
Ca or Cl	$CaCl_2$	55.5
Mg or CO_3	$MgCO_3$	42.2
Mg or SO_4	$MgSO_4$	60.1
Mg or Cl	$MgCl_2$	47.6
Fe or CO_3	$FeCO_3$	57.8
Fe or SO_4	$FeSO_4$	76.0
Fe or Cl	$FeCl_2$	63.4
Na or CO_3	Na_2CO_3	53.1
Na or SO_4	Na_2SO_4	71.0
Na or Cl	NaCl	58.4

The combination factors given in Table 5 can be used to calculate the hypothetical combinations shown in Table 6, using the analysis shown in Table 4.

Table 6. HYPOTHETICAL COMBINATIONS

$Ca(HCO_3)$ to $CaCO_3$	8.2 x 50.1 =	411 mg/l $CaCO_3$
$CaSO_4$	4.2 x 68.1 =	286 mg/l $CaSO_4$
$CaCl_2$	187.2 x 55.5 =	10,390 mg/l $CaCl_2$
$MgCl_2$	246.8 x 47.6 =	11,748 mg/l $MgCl_2$
$FeCl_2$	3.6 x 63.4 =	228 mg/l $FeCl_2$
NaCl	858.9 x 58.4 =	50,160 mg/l NaCl

GRAPHIC PLOTS

Graphic plots of the reacting values can be made to illustrate the relative amounts of each radical present. The graphical presentation is an aid to rapid identification of a water, and classification as to its type, and there are several methods that have been developed.

Tickell Diagram

The Tickell [4] diagram was developed by using a six-axis system or star diagram. Percentage reaction values of the ions are plotted on the axes. The percentage values are calculated by summing the epm's of all the ions, dividing the epm of a given ion by the sum of the total epm's, and multiplying by 100.

The Tickell diagram uses reaction values in percentage while total reaction values are used in the modified Tickell, Figure 1. The plots of total reaction values, rather than of percentage reaction values, are often more useful in water identification because the percentage values do not take into account the actual ion concentrations. Water differing only in concentrations of dissolved constituents cannot be distinguished.

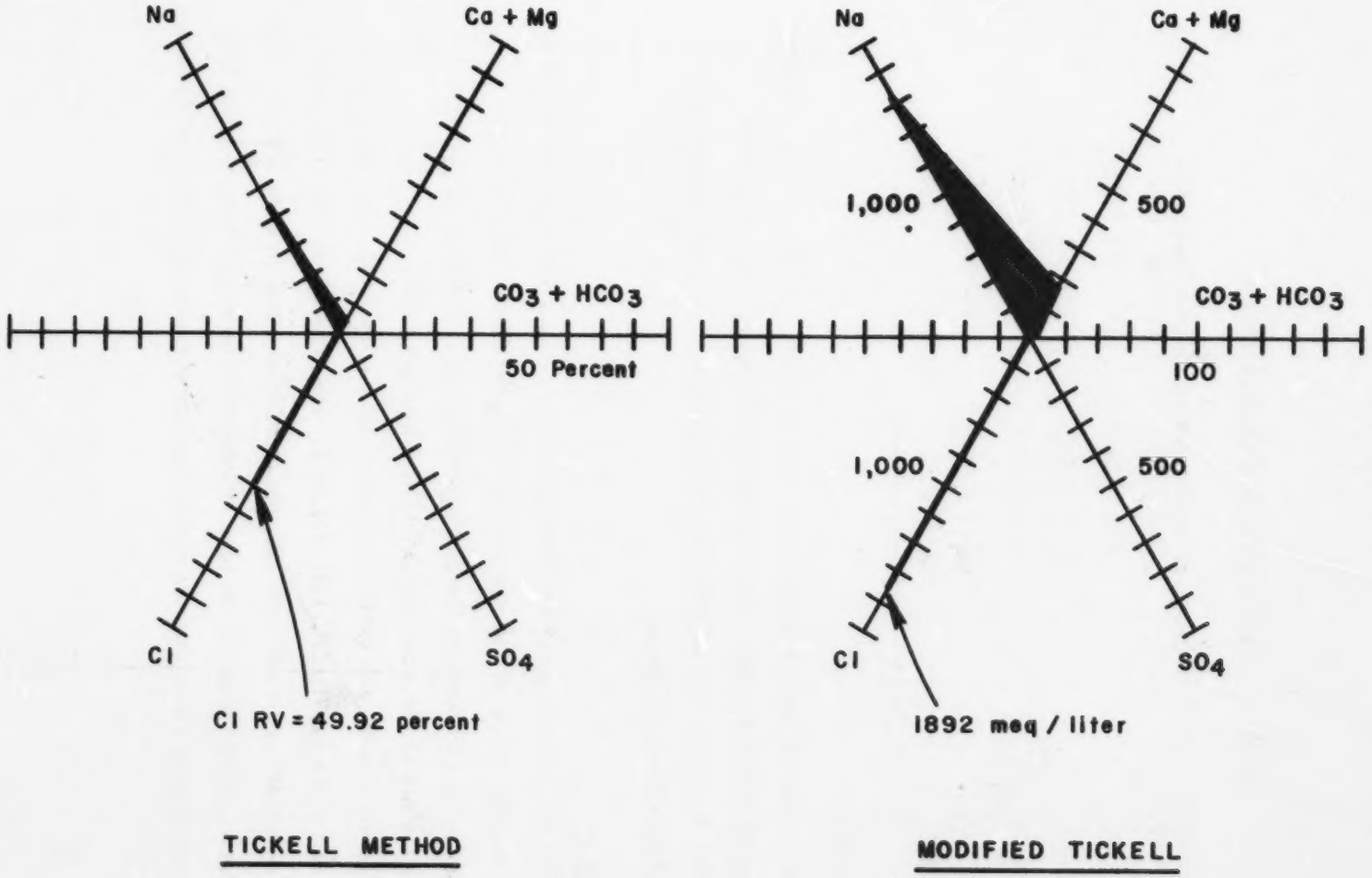


Figure 1. Tickell and modified Tickell diagram for Gulf Coast water, sample no. 1.

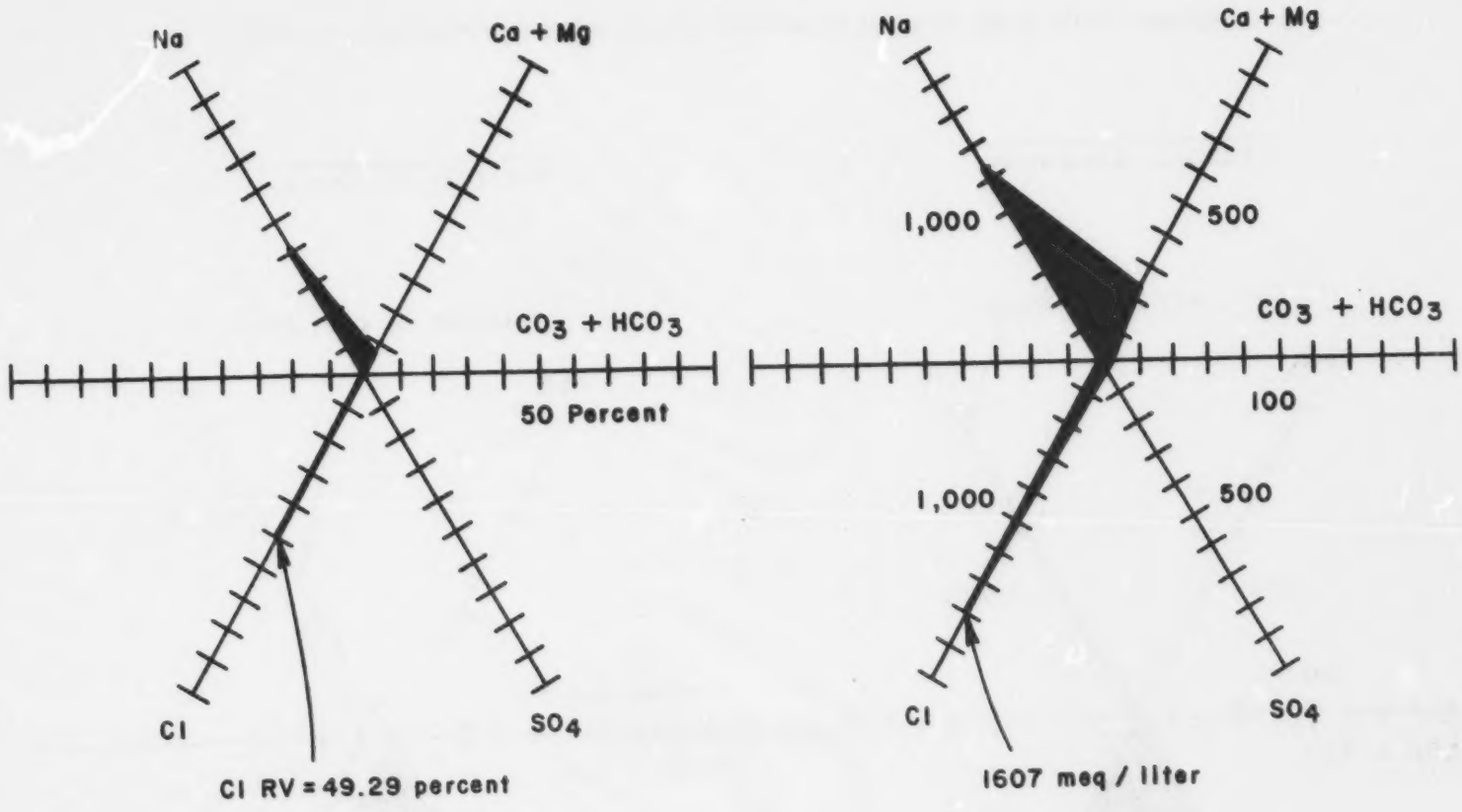


Figure 2. Tickell and modified Tickell diagram for Anadarko Basin water, sample no. 2.

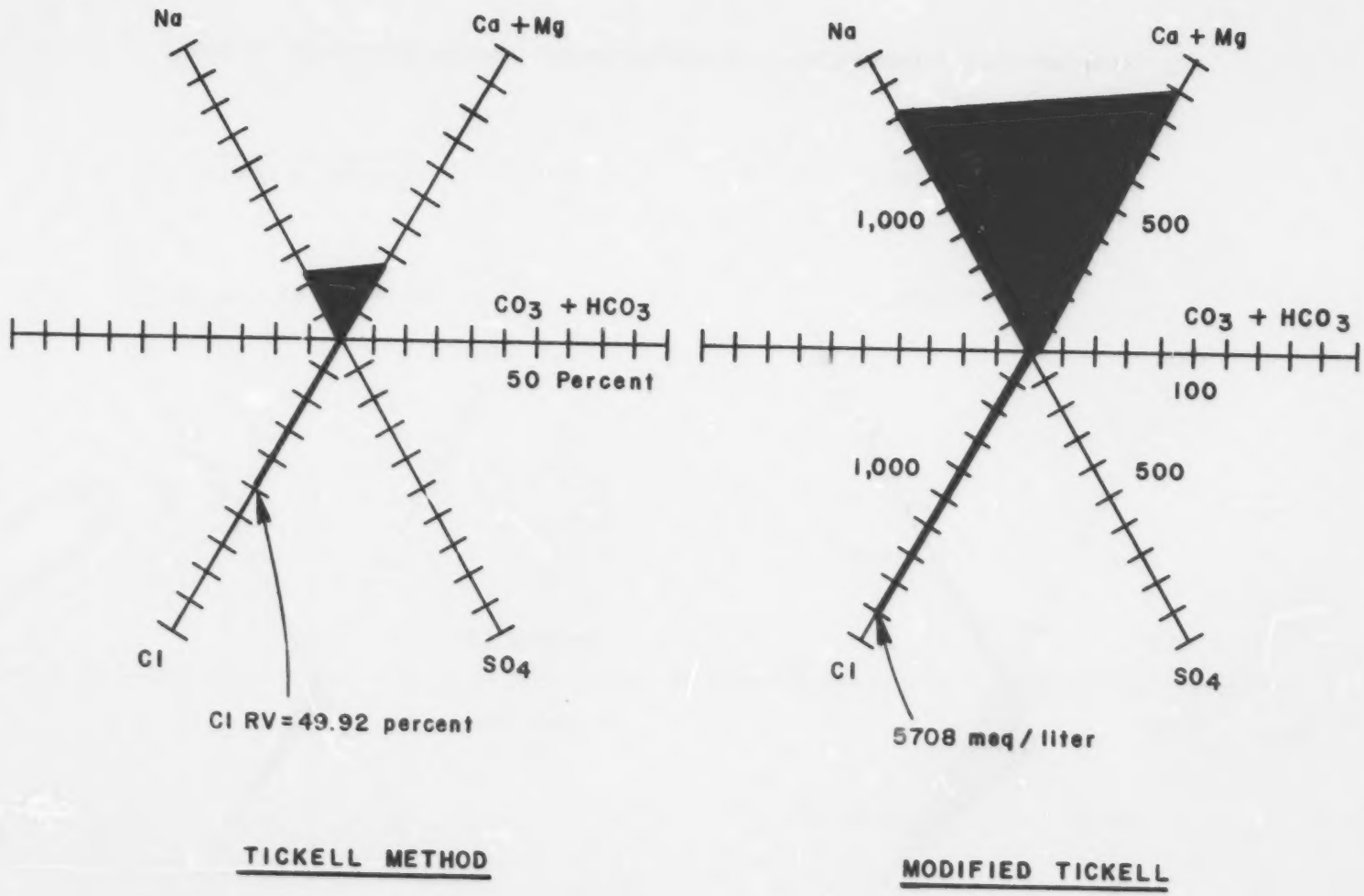


Figure 3. Tickell and modified Tickell diagram for Williston Basin water, sample no. 3.

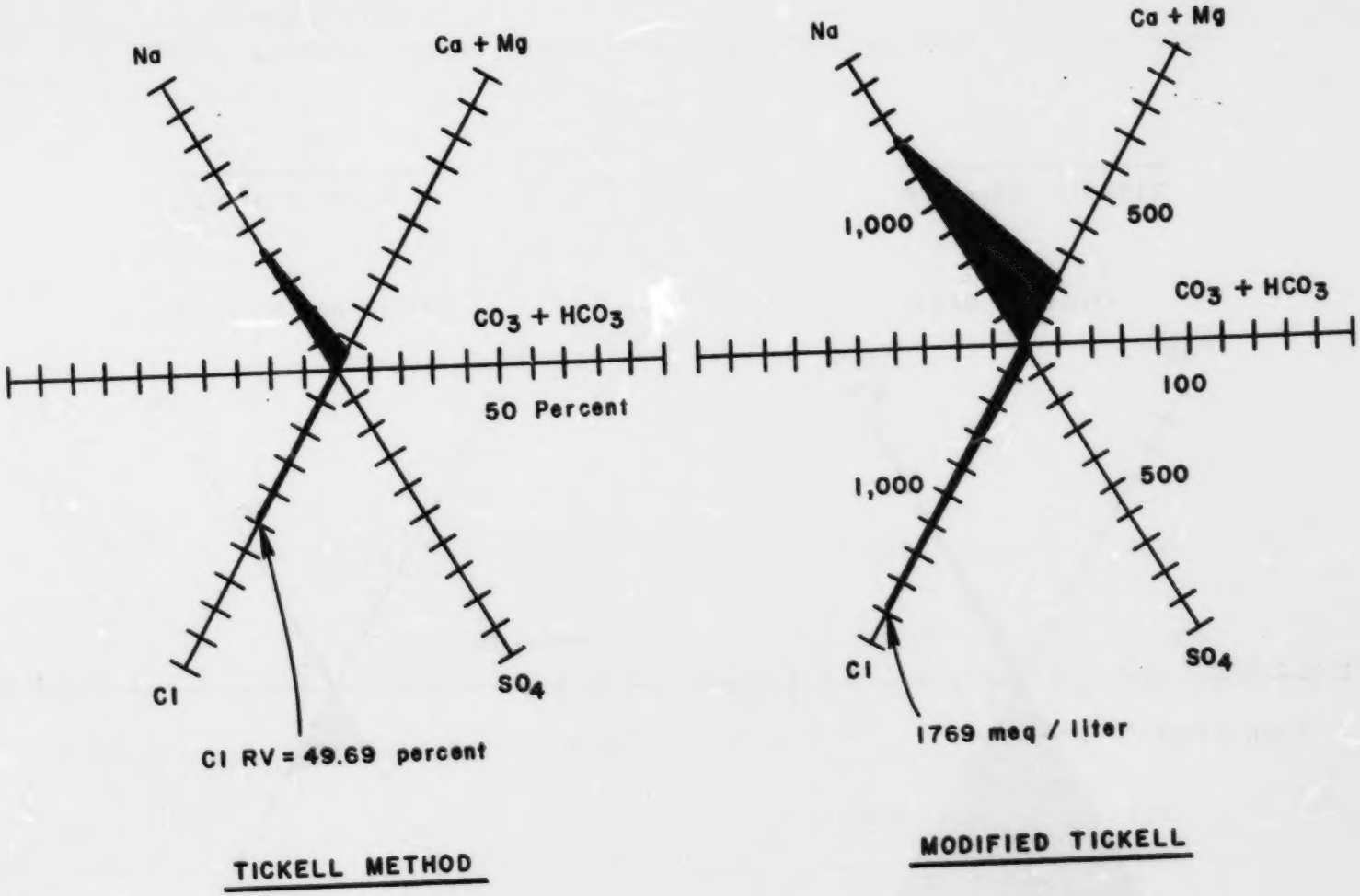


Figure 4. Tickell and modified Tickell diagram for Gulf Coast and Anadarko Basin waters, mixed 1 to 1.

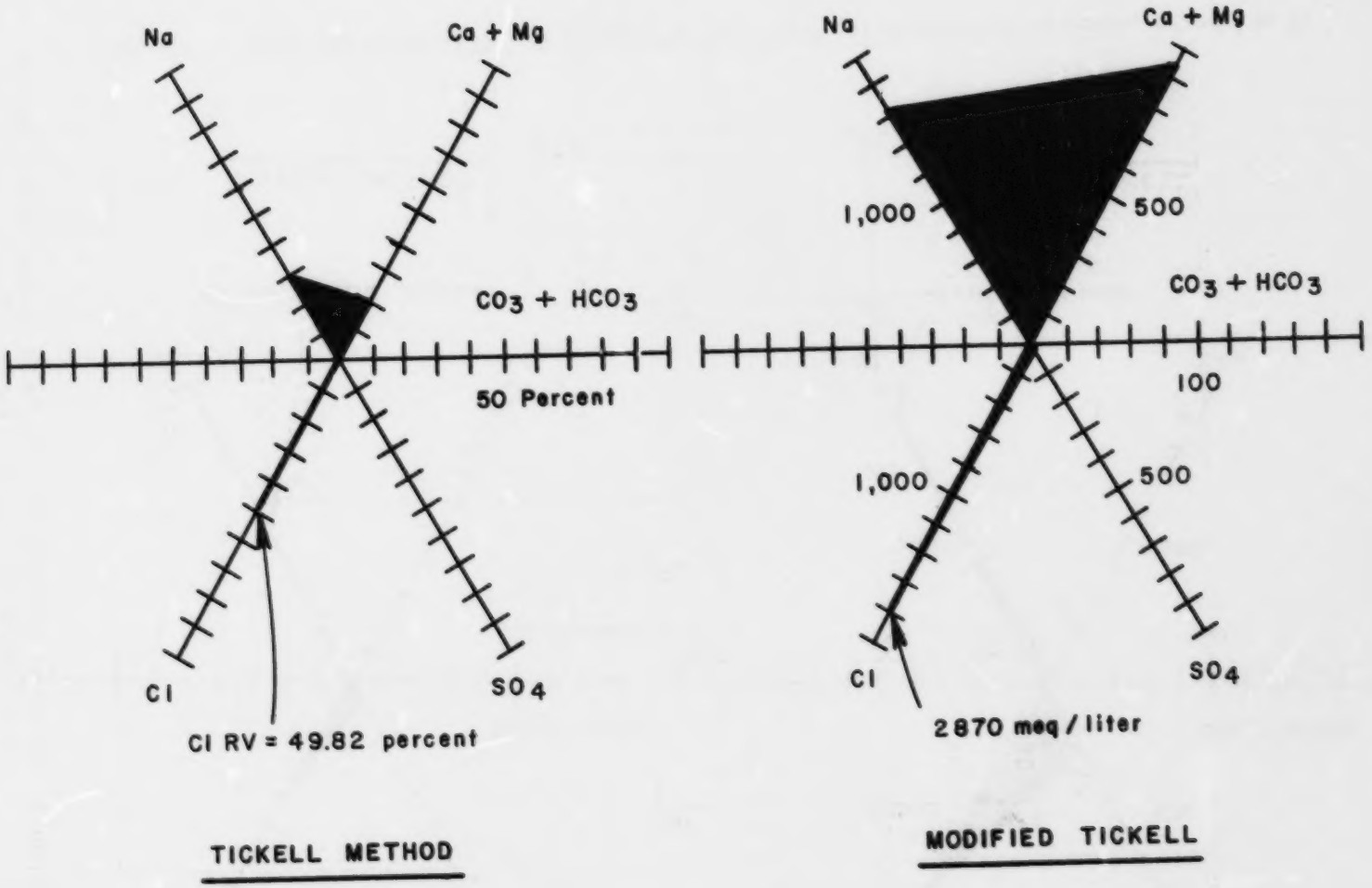


Figure 5. Tickell and modified Tickell diagram for Gulf Coast, Williston, and Anadarko Basin waters, mixed 1:1:1.

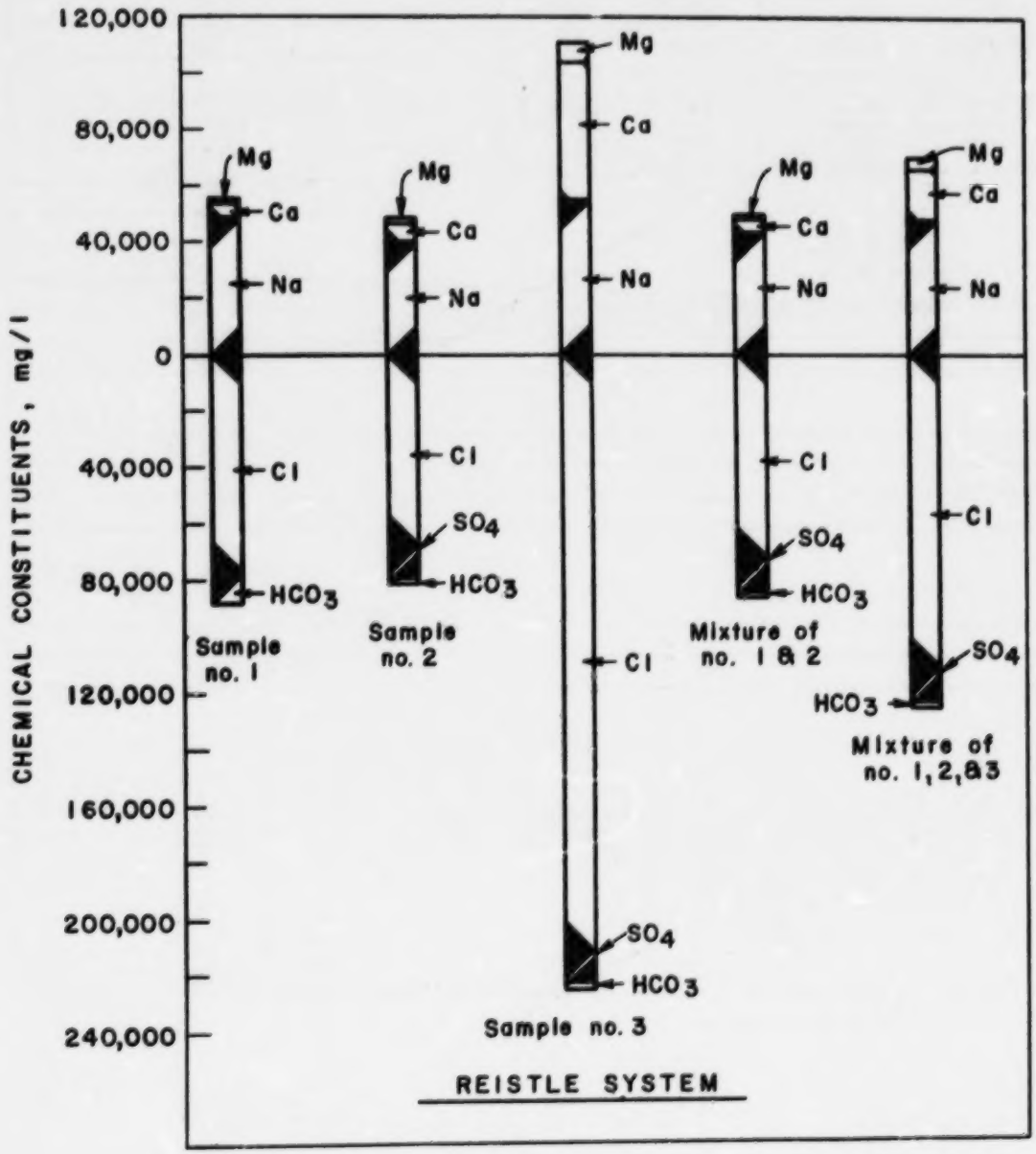


Figure 6. Water-analysis interpretation, Reistle system--sample numbers correspond to those shown on figures 1-3.

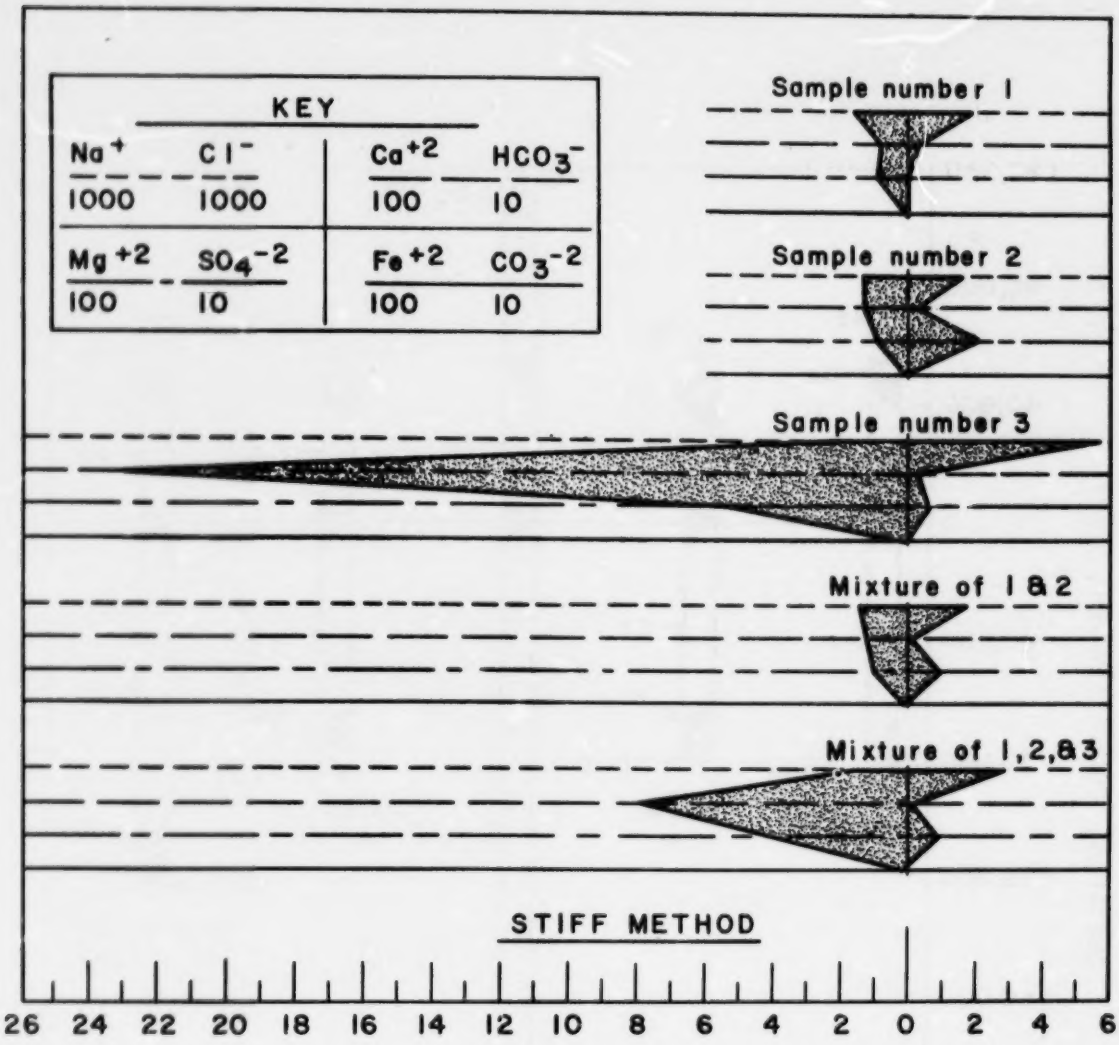


Figure 7. Water-analysis interpretation, Stiff method--sample numbers correspond to those shown on figures 1-3.

To illustrate differences in patterns for different waters, Figures 1-5 were prepared using the Tickell and modified Tickell methods. Figure 1 represents a water from the Gulf Coast Basin, taken from the Wilcox Formation of Eocene Age. Figure 2 is of a sample from the Meramec Formation of Mississippian Age in the Anadarko Basin. Figure 3 is of a sample from a Devonian Age Formation in the Williston Basin. Figure 4 represents a 1-to-1 mixture of waters of the Gulf Coast and Anadarko Basins, and Figure 5 is a 1-to-1 mixture of all three waters.

Reistle Diagram

Reistle[2] devised a method of plotting water analyses using the ion concentrations as shown in Figure 6. The data are plotted on a vertical diagram, with the cations plotted above the central zero line and the anions below. This type of diagram often is useful in making regional correlations or studying lateral variations in the water of a single formation, because several analyses can be plotted on a large sheet of paper.

Stiff Diagram

Stiff[3] plotted the reaction values of the ions on a system of rectangular coordinates as illustrated in Figure 7. The cations are plotted to the left and the anions to the right of a vertical zero line. The end points then are connected by straight lines to form a closed diagram, sometimes called a "butterfly" diagram. To emphasize a constituent that may be a key to interpretation, the scales may be varied by changing the denominator of the ion fraction usually in multiples of 10. However, when looking at a group of waters all must be plotted on the same scale.

Many investigators believe that this is the best method of comparing oilfield water analyses. The method is simple, and nontechnical personnel can be easily trained to construct the diagrams.

Automated Methods

The Piper[1] diagram and the Stiff[3] diagram were adapted to automatic data processing by Morgan, et al[5], and Morgan and McNellis[6]. The Piper[1] diagram

uses a multiple trilinear plot to depict the water analysis, and this quaternary diagram shows the chemical composition of the water in terms of cations and anions. Angino and Morgan[7] applied the automated Stiff[3] and Piper[1] diagrams to some oilfield brines and obtained good results.

SECTION VI

SALINE WATER CLASSIFICATION

Classification of waters provides a basis for grouping closely related waters. Because the grouping is chemical, it is dependent upon the dissolved constituents found in the waters. Most of the classification systems developed to date have considered only the dissolved major inorganic constituents and have ignored the organic and the minor and trace inorganic constituents.

Waters as related to the earth are meteoric, surface, and subsurface. Surface waters can be fresh or saline if the amounts of dissolved constituents in the waters are used to classify them. For example, water from melting snow on a mountain top usually will contain small amounts of dissolved mineral matter and can be classified as freshwater, while water in an ocean will contain about 35,000 milligrams per liter (mg/l) dissolved minerals and is classified as saline. Waters found in rivers connecting the mountain stream to the ocean may contain varying amounts of dissolved constituents and depending upon the amounts can be classified as fresh or saline. In a similar manner, subsurface waters are classified as fresh or saline. Merely classifying a water as either fresh or saline does not provide a very useful classification. The dissolved constituents that are used in many classification systems depend upon the amounts or ratios of sodium, magnesium, calcium, carbonate, bicarbonate, sulfate, and chloride found in the water. The reason for this is that these are the ions that usually are determined or calculated in a water. (Sodium often is calculated from the difference found in the stoichiometric balance of the determined anions and cations.)

The amounts and ratios of these constituents in subsurface waters are dependent upon the origin of the water and what has occurred to the water since entering the subsurface environment. For example, some subsurface waters found in deep

sediments were trapped during sedimentation while other subsurface waters have been diluted by infiltration of surface waters through outcrops. Some waters have been replaced by infiltration water. Also, rocks containing the waters often contain soluble constituents that dissolve in the waters or contain chemicals that will exchange with chemicals dissolved in the waters, causing alterations of the dissolved constituents.

The amounts of dissolved constituents found in subsurface waters can range from a few milligrams per liter to more than 350,000 mg/l. This salinity distribution is dependent upon several factors, including hydraulic gradients, depth of occurrence, distance from outcrops, mobility of the dissolved chemical elements, soluble material in the associated rocks, and the exchange reactions.

Several thousand saline waters were classified using automatic data processing. Table 7 illustrates some of the classification data for some of the samples from the Arbuckle and Lansing Kansas City Formations in the Central Kansas Basin; the Wilcox Formation in the Cherokee Basin; the Nacatoch, Paluxy, Rodessa, and Woodbine Formations in the East Texas Basin; the Eutaw Formation in the Interior Salt Basin; the Smackover Formation in the North Louisiana Basin; and the Wilcox Formation in the Western Gulf Basin. The majority of these waters fall in the $S_1S_2A_2$ class and are of the chloride-calcium type; Collins [8] explained these classes and types.

Most of the samples of the bicarbonate-sodium and sulfate-sodium types were found at relatively shallow depths. This indicates that the waters contain infiltrating meteoric water. The majority of the oilfield waters classified were very high-chloride waters (where chloride epm is equal to or greater than 700). The sulfate concentration of these waters according to this classification was not as consistent. Many of them were normal with sulfate epm less than 6. However, in several waters the sulfate epm was higher than 24. Few waters contained sulfate in excess of 58 epm. The $\sqrt{Ca \times SO_4}$ in epm units exceeded 70 in some waters, indicating

Table 7. CLASSIFICATION OF SOME SALINE GROUNDWATERS FROM 10 FORMATIONS IN EIGHT SEDIMENTARY BASINS

No.	State	Formation	Basin	Depth, meters	Concentration, EPM							Sulin		Schoeller				
					Na	Mg	Ca	HCO_3	SO_4	Cl	ΣEPM	Type	Class	Cl[a]	SO_4[b]	$\sqrt{Ca \cdot SO_4}$	$\sqrt[3]{(HCO_3 + CO_3)^2(Ca)}$	IBE
1	Kans.	Arbuckle	Cent. Kans.	1,050	634.6	60.6	133.0	7.7	49.0	773.8	1659.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(H)	80.7	20.0	0.18
2	Do.	do.	do.	1,091	581.6	58.4	121.8	6.5	22.7	732.3	1523.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	52.6	17.4	0.21
3	Do.	do.	do.	1,023	282.0	24.8	40.2	9.5	22.1	313.9	692.6	Cl-Ca	$S_1S_2A_2$	(H)C	(A)	29.8	15.4	0.10
4	Do.	do.	do.	1,102	639.9	56.6	13.0	2.2	46.6	827.0	1585.4	Cl-Ca	$S_1S_2S_3$	(VH)C	(H)	77.8	8.7	0.23
5	Do.	do.	do.	992	430.3	38.8	65.4	8.5	17.5	510.9	1071.6	Cl-Ca	$S_1S_2A_2$	(H)C	(A)	33.8	16.8	0.16
6	Do.	do.	do.	1,152	458.7	34.4	81.3	3.4	45.9	523.2	1147.2	Cl-Ca	$S_1S_2A_2$	(M)C	(H)	61.1	9.9	0.12
7	Do.	do.	do.	1,174	473.2	53.1	119.4	5.1	36.0	705.0	1492.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(H)	65.6	14.6	0.19
8	Do.	do.	do.	949	356.4	57.4	100.4	12.8	39.9	456.7	1684.0	Cl-Ca	$S_1S_2A_2$	(M)C	(H)	62.3	25.2	0.22
9	Do.	do.	do.	1,195	446.4	35.4	71.2	9.0	30.0	512.7	1185.0	Cl-Ca	$S_1S_2A_2$	(M)C	(H)	46.2	17.9	0.13
10	Do.	do.	do.	1,104	577.4	49.4	112.1	35.9	45.5	685.8	1506.4	Cl-Ca	$S_1S_2A_2$	(M)C	(H)	71.4	52.5	0.16
11	Do.	Lansing	do.	928	1759.6	266.6	373.9	1.8	0.0	2398.9	4800.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	10.7	0.27
12	Do.	do.	do.	1,075	570.4	117.4	174.6	2.4	34.9	826.6	1726.4	Cl-Ca	$S_1S_2A_2$	(VH)C	(H)	78.0	10.2	0.31
13	Do.	do.	do.	966	1899.9	266.4	442.1	0.3	0.8	2605.0	5214.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	19.4	3.5	0.27
14	Do.	do.	do.	999	1728.2	232.0	512.4	1.7	2.5	2469.4	4946.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	36.0	11.6	0.30
15	Do.	do.	do.	902	1903.0	274.5	478.8	1.1	0.0	2655.6	5314.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	8.5	0.28
16	Do.	do.	do.	1,009	2514.8	309.3	532.7	0.4	1.5	3353.6	6712.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	28.7	4.4	0.25
17	Do.	do.	do.	1,063	1854.7	225.2	449.8	0.5	1.1	2529.5	5061.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	22.5	5.1	0.27
18	Do.	do.	do.	1,148	2087.2	223.6	384.8	1.4	1.0	2706.1	5404.4	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	20.4	9.1	0.23
19	Do.	do.	do.	1,172	2414.5	251.0	519.0	0.7	2.4	3179.9	6367.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	35.9	6.3	0.24
20	Do.	do.	do.	853	1898.4	270.8	416.7	0.8	0.7	2515.5	5043.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	17.8	6.6	0.25
21	Okla.	Wilcox	Cherokee	1,228	2366.5	193.3	810.1	1.1	7.7	3360.6	6739.4	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	79.1	9.9	0.30
22	Do.	do.	do.	1,731	2188.4	209.5	529.4	0.3	9.8	2917.2	5854.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	72.3	3.6	0.25
23	Do.	do.	do.	904	2161.5	163.2	530.3	0.4	7.3	2847.4	5710.4	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	62.3	4.7	0.24
24	Do.	do.	do.	1,539	2365.3	200.8	445.6	1.1	15.9	2992.0	6021.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	84.3	8.5	0.21
25	Do.	do.	do.	1,106	1997.1	140.4	457.3	0.9	7.8	2584.3	5188.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	59.9	7.1	0.23
26	Do.	do.	do.	1,020	1990.0	161.3	513.7	0.7	13.3	2650.8	5330.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	82.7	6.4	0.25
27	Do.	do.	do.	582	1587.2	151.2	287.5	1.8	1.4	2021.6	4051.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	20.5	9.9	0.21
28	Do.	do.	do.	1,432	2459.0	174.5	511.6	1.1	6.0	3138.8	6291.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	55.7	8.7	0.22
29	Do.	do.	do.	1,972	2701.4	153.1	606.0	0.7	8.4	3449.1	6918.8	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	71.4	7.1	0.22
30	Do.	do.	do.	1,865	2635.5	180.6	629.6	1.1	8.6	3436.6	6892.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	73.6	9.4	0.23
31	Ark.	Nacatoch	E. Texas	360	233.4	9.0	22.4	3.7	0.0	261.1	529.8	Cl-Ca	$S_1S_2A_2$	(H)C	(N)	0.6	6.8	0.11
32	Do.	do.	do.	465	463.4	39.5	59.5	1.4	0.0	559.5	1123.5	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	0.0	4.9	0.17
33	Do.	do.	do.	373	300.4	25.9	36.8	4.3	1.0	357.7	726.2	Cl-Ca	$S_1S_2A_2$	(H)C	(N)	6.0	8.8	0.16
34	Tex.	do.	do.	905	788.2	9.4	28.7	3.1	0.0	824.6	1654.2	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	6.5	0.04
35	Do.	do.	do.	701	481.8	7.8	17.3	3.3	0.0	503.5	1013.8	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	0.0	5.7	0.04
36	Do.	do.	do.	242	274.0	8.1	14.7	2.5	0.8	294.2	594.5	Cl-Ca	$S_1S_2A_2$	(H)C	(N)	3.6	4.6	0.07
37	Do.	do.	do.	650	492.7	10.4	16.5	18.9	0.1	498.4	1037.4	Cl-Mg	$S_1A_2S_3$	(M)C	(N)	1.6	18.1	0.01
38	Do.	do.	do.	283	295.4	8.1	14.7	2.4	0.9	313.6	635.2	Cl-Ca	$S_1S_2A_2$	(H)C	(N)	3.6	4.4	0.06
39	Do.	do.	do.	191	451.5	17.6	44.7	7.1	0.4	506.2	1027 8	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	4.5	13.2	0.11
40	Do.	do.	do.	181	490.6	3.6	7.8	2.8	0.6	498.4	1004.0	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	2.2	4.0	0.02

Table 7 (continued). CLASSIFICATION OF SOME SALINE GROUNDWATERS FROM 10 FORMATIONS IN EIGHT SEDIMENTARY BASINS

No.	State	Formation	Basin	Depth, meters	Concentration, EPM							Sulin		Schoeller				
					Na	Mg	Ca	HCO_3	SO_4	Cl	ΣEPM	Type	Class	Cl[a]	SO_4[b]	$\sqrt{Ca \cdot SO_4}$	$\sqrt[3]{(HCO_3 + CO_3)^2 (Ca)}$	IBE
41	Ark.	Paluxy	E. Texas	1,115	1246.8	90.6	254.1	0.4	0.0	1594.4	3186.6	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	3.1	3.8	0.22
42	Do.	do.	do.	737	586.0	32.2	86.7	2.8	3.3	699.0	1410.3	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	17.1	8.8	0.16
43	Do.	do.	do.	1,297	1310.3	107.1	278.5	2.7	0.7	1692.0	3391.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	14.1	12.8	0.23
44	Do.	do.	do.	884	934.9	64.8	197.6	1.5	1.1	1194.9	2395.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	15.0	7.6	0.22
45	Do.	do.	do.	1,417	1507.2	138.6	504.4	0.5	3.3	2208.7	4363.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	41.0	5.4	0.29
46	Tex.	do.	do.	2,340	1642.1	22.5	378.5	0.0	9.3	2033.8	4086.4	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	59.5	0.0	0.19
47	Do.	do.	do.	2,174	1515.1	51.1	205.9	4.7	3.7	1763.1	3543.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	27.9	16.6	0.14
48	Do.	do.	do.	1,943	1495.4	89.0	448.9	2.7	8.2	2022.2	4066.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	60.9	13.6	0.26
49	Do.	do.	do.	1,512	205.3	6.4	10.0	14.9	6.0	202.4	445.2	SO_4-Na	$S_1A_2S_3$	(M)C	(A)	7.7	13.1	0.0
50	Do.	do.	do.	1,943	1522.8	90.2	448.1	1.8	8.3	2050.3	4121.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	61.0	11.1	0.26
51	Ark.	Rodessa	E. Texas	1,897	1971.8	157.2	669.7	0.0	8.0	2789.9	5596.8	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	73.3	0.5	0.29
52	Do.	do.	do.	1,241	1943.8	185.1	563.6	0.9	11.7	2679.0	5384.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	81.3	8.0	0.27
53	Do.	do.	do.	1,033	1060.3	108.2	289.8	0.0	21.4	1436.5	2916.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	78.7	0.4	0.26
54	Do.	do.	do.	711	538.6	35.9	75.0	3.0	2.9	643.4	1299.0	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	14.8	8.8	0.16
55	Tex.	do.	do.	2,844	1772.1	147.3	878.8	1.5	2.8	2773.2	5556.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	50.1	12.9	0.36
56	Do.	do.	do.	2,519	1861.9	217.4	1084.7	1.1	2.7	3145.1	6333.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	54.4	11.1	0.41
57	Do.	do.	do.	2,722	2068.5	148.5	900.9	0.6	4.8	3111.6	6235.2	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	66.2	7.3	0.34
58	Do.	do.	do.	2,115	1950.3	132.9	726.1	1.8	8.5	2802.4	5622.2	Cl-Ca	$S_1S_2S_3$	(VH)C	(A)	79.0	13.5	0.30
59	Do.	do.	do.	2,289	2020.0	141.2	741.8	0.8	4.2	2909.8	5818.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	55.9	7.7	0.31
60	Do.	do.	do.	3,062	1877.5	92.7	610.0	1.0	5.4	2576.9	5163.7	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	57.4	8.4	0.27
61	Do.	Woodbine	do.	1,047	1507.0	44.3	161.4	4.2	3.5	1705.0	3425.6	Cl-Ca	$S_1S_2A_2$	(VH)(C)	(N)	23.9	14.2	0.12
62	Do.	do.	do.	1,750	1263.0	33.4	56.3	8.2	1.8	1342.2	2705.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	10.0	15.6	0.06
63	Do.	do.	do.	898	341.8	4.4	9.3	11.3	0.6	343.5	711.0	Cl-Mg	$S_1A_2S_3$	(H)C	(N)	2.4	10.6	0.00
64	Do.	do.	do.	841	1060.5	32.4	58.9	0.0	0.2	1161.4	2313.7	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	4.0	0.0	0.09
65	Do.	do.	do.	1,809	1271.9	59.6	154.9	1.0	4.9	1478.2	2970.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	27.6	5.4	0.14
66	Do.	do.	do.	1,144	809.1	12.7	61.1	7.3	3.7	873.3	1767.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	15.1	14.8	0.07
67	Do.	do.	do.	925	478.8	12.4	23.6	7.0	0.1	507.7	1029.9	Cl-Ca	$S_1S_2A_2$	(M)C	(N)	1.5	10.5	0.06
68	Do.	do.	do.	1,442	1451.3	26.7	213.3	3.9	0.0	1685.1	3379.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	14.8	0.14
69	Do.	do.	do.	1,596	1447.3	38.3	144.1	1.6	0.1	1629.4	3261.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	3.7	7.4	0.11
70	Do.	do.	do.	1,332	1268.0	30.2	81.9	8.3	4.0	1367.4	2760.0	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	18.1	17.8	0.07
71	Ala.	Eutaw	Interior Sal.	1,061	1124.4	45.0	164.7	2.7	0.0	1330.1	2667.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.1	10.6	0.15
72	Do.	do.	do.	972	1102.9	25.6	160.5	2.0	0.0	1288.9	2580.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.1	8.8	0.14
73	Do.	do.	do.	1,060	1186.7	59.6	164.3	2.9	0.0	1411.8	2825.4	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.1	11.1	0.16
74	Miss.	do.	do.	1,444	1733.6	82.7	287.3	0.9	0.0	2108.5	4213.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.1	6.2	0.18
75	Do.	do.	do.	2,263	2009.8	75.9	306.8	5.2	33.6	2358.5	4789.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(H)	101.6	20.3	0.15
76	Do.	do.	do.	1,312	1572.7	88.9	224.9	0.9	0.0	1890.2	3777.7	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.0	5.7	0.17
77	Do.	do.	do.	2,443	1721.3	256.7	458.0	0.0	0.0	2433.4	4869.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	0.0	0.29
78	Do.	do.	do.	1,690	1925.9	61.6	359.9	3.9	0.0	2352.4	4704.8	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.0	17.8	0.18
79	Do.	do.	do.	1,315	1579.6	60.6	252.9	2.3	0.0	1893.5	3789.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.0	11.0	0.17
80	Do.	do.	do.	2,469	2153.7	87.7	518.9	0.0	1.0	2765.6	5527.1	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	22.7	0.0	0.22

Table 7 (continued). CLASSIFICATION OF SOME SALINE GROUNDWATERS FROM 10 FORMATIONS IN EIGHT SEDIMENTARY BASINS

No.	State	Formation	Basin	Depth, meters	Concentration, EPM							Sulin		Schoeller				
					Na	Mg	Ca	HCO_3	SO_4	Cl	Σ EPM	Type	Class	Cl[a]	SO_4[b]	$\sqrt{Ca \cdot SO_4}$	$\sqrt[3]{(HCO_3 + CO_3)^2(Ca)}$	IBE
81	Miss.	Wilcox	Miocene	1,975	2031.8	36.8	100.3	4.5	0.0	2163.3	4336.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	12.7	0.06
82	Do.	do.	do.	1,748	1867.9	48.4	94.9	3.8	0.0	1985.9	3981.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	11.2	0.07
83	Do.	do.	do.	1,412	1362.9	15.0	82.5	4.4	0.0	1455.8	2920.8	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	11.8	0.06
84	Do.	do.	do.	1,871	2157.3	54.1	89.9	6.8	0.0	2114.0	4422.4	HCO_3-Na	$S_1A_2A_1$	(VH)C	(N)	0.0	16.1	0.0
85	Do.	do.	do.	2,330	1972.2	65.8	95.7	3.9	7.2	2122.3	4367.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	26.2	11.4	0.7
86	Do.	do.	do.	1,646	1992.4	38.0	81.9	3.0	0.0	2108.5	4223.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	9.0	0.06
87	Do.	do.	do.	2,162	2043.7	25.5	132.2	7.2	0.0	2194.5	4403.4	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.1	18.9	0.07
88	Do.	do.	do.	2,268	2198.7	83.8	90.7	3.9	0.3	2369.8	4747.3	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	5.4	11.1	0.07
89	Do.	do.	do.	1,552	1280.8	36.7	56.3	9.4	0.0	1364.3	2747.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	17.0	0.06
90	Do.	do.	do.	1,327	1318.9	20.9	99.6	3.9	0.0	1434.8	2878.2	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	11.5	0.08
91	La.	Smackover	N. Louis	3,109	1589.7	86.7	1256.8	0.0	8.8	2940.8	5883.0	Cl-Ca	$S_1S_2S_3$	(VH)C	(A)	103.6	0.0	0.46
92	Ark.	do.	do.	2,103	2444.9	275.9	1392.8	2.0	4.6	4105.9	8226.2	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	80.0	17.7	0.40
93	Do.	do.	do.	2,399	2518.1	280.4	1622.1	1.8	3.7	4413.8	8840.1	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	78.0	17.9	0.43
94	Do.	do.	do.	2,509	2790.1	222.2	1641.6	2.3	1.7	4648.6	9306.8	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	53.5	21.1	0.40
95	Do.	do.	do.	2,240	2418.0	279.5	1478.8	0.8	4.1	4163.0	8335.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	78.0	0.6	0.42
96	Do.	do.	do.	2,526	2729.0	218.6	1598.2	2.4	1.7	4540.4	4545.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	53.4	21.3	0.40
97	Do.	do.	do.	2,615	4277.5	10.0	34.9	2.4	0.0	4312.9	8637.9	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	5.9	0.01
98	La.	do.	do.	2,949	2225.4	149.7	2282.1	0.0	1.4	4654.9	9313.8	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	57.5	0.7	0.52
99	Do.	do.	do.	3,271	1971.2	173.5	1668.9	0.0	1.8	3810.9	7626.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	55.5	0.6	0.48
100	Do.	do.	do.	701	681.8	35.2	63.6	5.1	2.1	778.6	1566.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	11.4	11.6	0.12
101	Do.	Wilcox	W. Gulf	1,399	1718.5	44.9	90.1	1.4	0.2	1851.2	3706.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	5.1	5.6	0.07
102	Do.	do.	do.	1,814	2035.8	46.5	124.7	5.6	0.8	2199.9	4413.6	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	10.2	15.8	0.07
103	Do.	do.	do.	747	1206.3	43.6	47.2	4.6	0.6	1291.2	2593.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	5.6	10.1	0.07
104	Do.	do.	do.	1,561	1874.2	40.9	91.0	0.7	0.8	2003.8	4011.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	8.8	3.6	0.06
105	Do.	do.	do.	1,722	2138.9	41.9	96.2	1.4	1.4	2273.4	4553.5	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	11.7	5.9	0.06
106	Do.	do.	do.	666	1057.5	26.6	51.0	0.0	0.0	1058.4	2193.6	Cl-Mg	$S_1A_2S_2$	(VH)C	(N)	0.0	0.0	0.0
107	Do.	do.	do.	1,124	1379.4	41.8	60.0	2.5	0.6	1477.6	2962.2	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	6.1	7.3	0.07
108	Do.	do.	do.	2,441	2119.4	43.7	100.2	6.1	0.0	2263.8	4533.4	Cl-Ca	$S_1S_2S_3$	(VH)C	(N)	0.0	15.2	0.06
109	Do.	do.	do.	2,158	2132.3	15.3	115.2	4.0	8.0	2256.4	4531.3	Cl-Ca	$S_1S_2S_3$	(VH)C	(A)	29.9	12.1	0.05
110	Do.	do.	do.	471	840.1	26.8	24.1	7.0	0.0	888.4	1786.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(N)	0.0	9.9	0.05
111	N.Dak.	Silurian	Williston	3,633	3431.2	100.6	993.7	1.5	8.4	4305.3	8840.7	Cl-Ca	$S_1S_2A_2$	(VH)C	(A)	90.6	13.0	0.20

[a] epm Cl is > 700, (VH)C
epm Cl is 420 to 700, (M)C
epm Cl is 140 to 420, (H)C
epm Cl is 40 to 140, (A)C
epm Cl is 10 to 40, (L)C
epm Cl is < 10, (N)C

[b] epm SO_4 is > 58, (VH)
epm SO_4 is 24 to 58, (H)
epm SO_4 is 6 to 24, (A)
epm SO_4 is < 6, (N)

that such waters were nearly saturated with calcium sulfate. The solubility of calcium sulfate increases in the presence of certain other dissolved ions, therefore the value of 70 may not always indicate saturation.

The $\sqrt[3]{(HCO_3 + CO_3)^2 (Ca)}$ in epm units is used to determine if a water is saturated with calcium carbonate, and such a water should have a value greater than 7. This is not entirely accurate, but the calculated value from the cubed root expression does indicate the presence of an excess of calcium which decreases the carbonate concentration. Many of the waters classified had values greater than 7. A distilled water thus saturated would deposit precipitated calcium carbonate, but the activities of other ions dissolved in a brine cause the solubility product to be different in the brine.

The predominant cation sequence for the classified oilfield brines was Na > Ca > Mg. The anion ratios of SO_4/Cl ranged from 0.00 to 0.34. The ratio 0.34 found for a bicarbonate-sodium type of water strongly indicates infiltrating surface water. None of the chloride-calcium type waters had a SO_4/Cl ratio greater than 0.17.

The index of base exchange (IBE), given in Table 7, indicates that exchange of metal ions dissolved in the water has occurred with metal ions on the clays.[8] If the IBE is a positive number, the exchange was alkali metals such as sodium in the water for alkaline earth metals such as calcium on the clays, and if the IBE is negative, the exchange was alkaline earth metals in the water for alkali metals on the clays. Very few negative numbers were evident when the IBE was determined on the oilfield water analyses. This indicates that most of these saline formation waters have exchanged alkali metals for alkaline earth metals on the clays. The few samples that yielded the negative IBE numbers were sulfate-sodium and bicarbonate-sodium type waters, which is indicative of terrestrial waters.

SECTION VII

PLOTTING SALINITY MAPS FOR USE IN LOCAL OR REGIONAL STUDIES

A study of stratigraphic problems within a subsurface formation was made by the use of saline formation waters. Over 300 samples of formation water were collected and analyzed. The results were processed by computer techniques. Data collected in this manner were posted on maps and machine contoured. Several aspects of the waters (relative percentages of SO_4, Mg, Ca, and total solids) show systematic variations in the basin. Variation in these parameters is related to proximity to outcrop and the degree of transmissibility of the formation. The highest sulfate content is near the outcrop belt to the west; the calcium and total solids increase toward more impermeable rocks and areas of low circulation. In the center of the basin the waters are characterized by very high salinities, high calcium and low sulfate content, but in the porous and permeable fingers near the outcrop, salinities are low and sulfate is high. All gradations between these two extremes exist in the example formation. In areas where the sand fingers pinch out very rapidly into low permeability sediments, the transition between these two extremes of water composition may take place in a matter of a few well locations. An excellent example of this is illustrated by Figures 8-10,[9] where a range of waters is evidenced in one homogeneous, continuous sand body. Note that the spot locations are divided by 100, while the contour lines are not.

The reason for these rapid changes in formation water composition may be explained by permeability changes within the subsurface formation. In areas of low permeability there is less circulation, less dilution, and more chance for the maintenance of an equilibrium relation between formation water and sediment. This was substantiated by the distribution of magnesium in the formation waters.

A series of multiple-regression analyses were made to determine the relation of the percent of various ions dissolved in the waters to the total solids dissolved

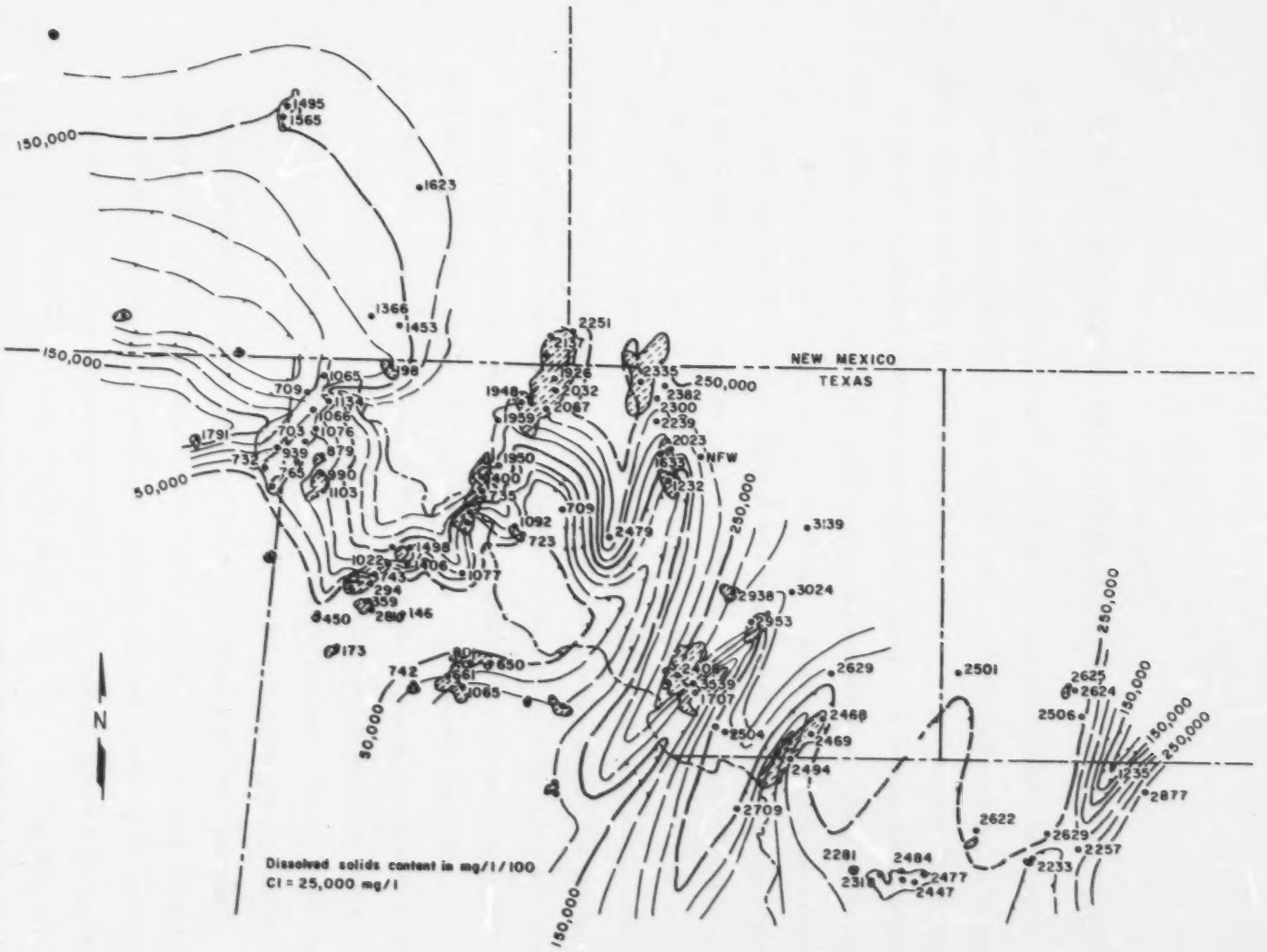


Figure 8. Concentrations of dissolved solids in the formation waters.[9]

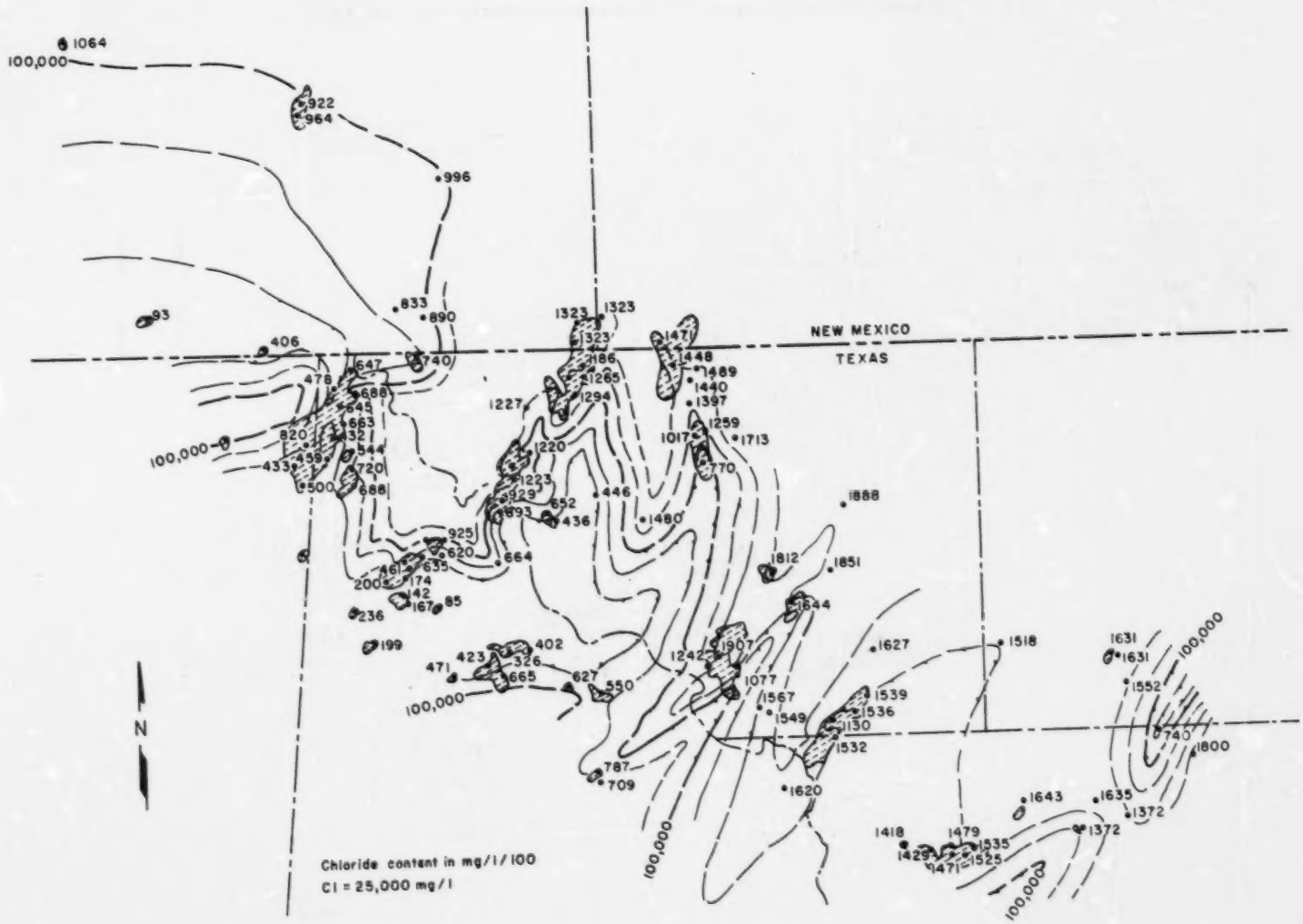


Figure 9. Chloride concentration in the formation waters.[9]

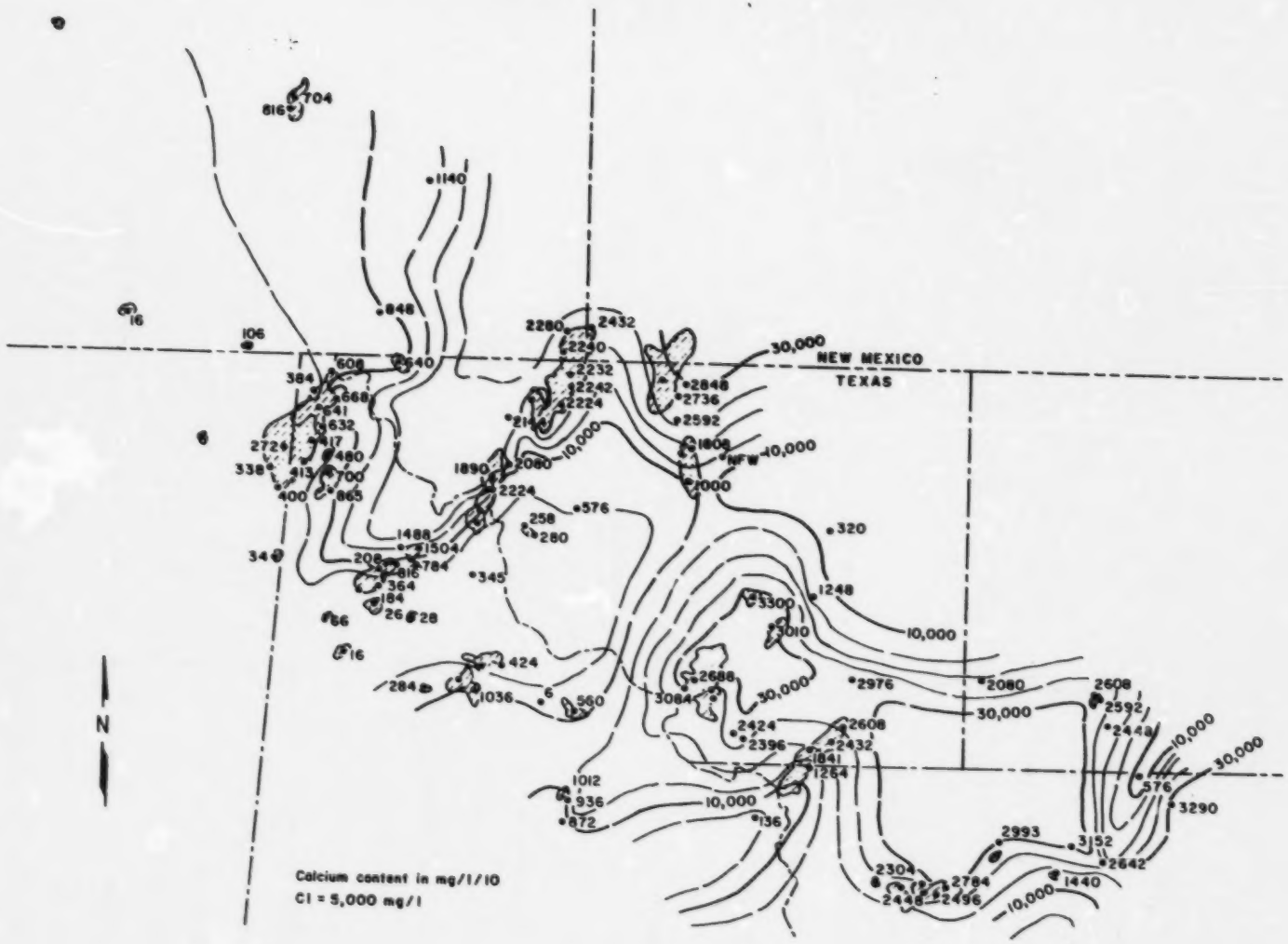


Figure 10. Calcium concentration in the formation waters.[9]

in the waters. First, all the waters were analyzed as a unit to determine the correlation coefficients and the degree of variability explained by the ions chosen for analysis. The second stage was the breakdown of the waters into three arbitrarily defined groups (based principally on salinities) to see if there were any noticeable changes in either correlation coefficients or degree of explained variance. The only significant change was in the relation of magnesium to total solids; i.e., in waters of relatively low salinity, there was a significant positive correlation to total dissolved solids, but in waters with high dissolved solids concentrations there was a significant negative correlation. These correlations indicate that the relative concentration of magnesium decreases in high-salinity waters. These waters are precisely those that are found in low-permeability, fine-grained, argillaceous rocks in which magnesium would most likely be taken out of the waters by diagenetic alteration of clay mineral.

Maps of the dissolved solids content, Figure 8, the chloride content, Figure 9, and the calcium content, Figure 10, of formation waters were prepared. It is important to note on each of the constituent maps that the local variation of the iso-mg/l contours are of greatest importance and not the precise value of the contour. For example, on the dissolved solids map, Figure 8, note that the overall appearance is a series of fingering expressions shown by the contour lines.

The chloride map, Figure 9, has a configuration similar to the total solids map. Again it is not the precise iso-mg/l contour that is of prime concern, but the variation in the limited area. This rate of change from higher to lower concentration is important in studying zones for subsurface disposal of waste; i.e., the lower concentration may indicate an outcrop.

The calcium content map, Figure 10, does not show the prominent fingering, almost pseudodeltaic, effect that the total solids and chloride maps have. Perhaps this is due to the smaller range of values mapped. Some of the high to lower concentration effect is present and in some of the locales, iso-mg/l closure is developed.

This map is not as diagnostic as the others. However, considered in conjunction with the other two maps, the coexistence of various salinity accumulations and the transition zones, even strata closure is quite evident.

The formation water constituent maps are definitely of value. Consideration of these with rock properties and hydrodynamic gradients permits the studying the potential of a disposal zone more accurately and will also permit meaningful extrapolation of inference with a minimum of data. The principal prerequisite for mapping reservoir trends such as sand fingers is the development of a detailed stratigraphic correlation. In deep subsurface water environments, as a rule, correlations are excellent because there is little variability in sedimentary environments. This can be substantiated by specific recognizable gamma ray markers on well logs.

Figure 11 is a map that illustrates the variation in salinity in the Lower Wilcox Formation in portions of Texas, Louisiana, Arkansas, Mississippi, and Alabama. The most saline brines occur in the deeper basin areas with the dilute brines nearer outcrop areas. The low-salinity waters near the coast cannot easily be attributed to intruding seawater because their salinity often is less than normal seawater. Pressure data are needed to determine if these waters are related to abnormally pressured zones such as those found in certain areas of Louisiana and elsewhere. Figure 12 is a similar map of the Lower Tuscaloosa and Woodbine Formations with no differentiation being given between the two.

The saline water data entered into STORET will prove of immense value in studies related to groundwater pollution and subsurface disposal of wastes. As noted, diagrams useful in water identification have been adapted to automatic data processing, and the saline water data in STORET can be used for this type of application. Water classification systems have been adapted to automatic data processing and the saline water data in STORET can be classified and studied to determine where certain types of saline waters are more prevalent. The class,

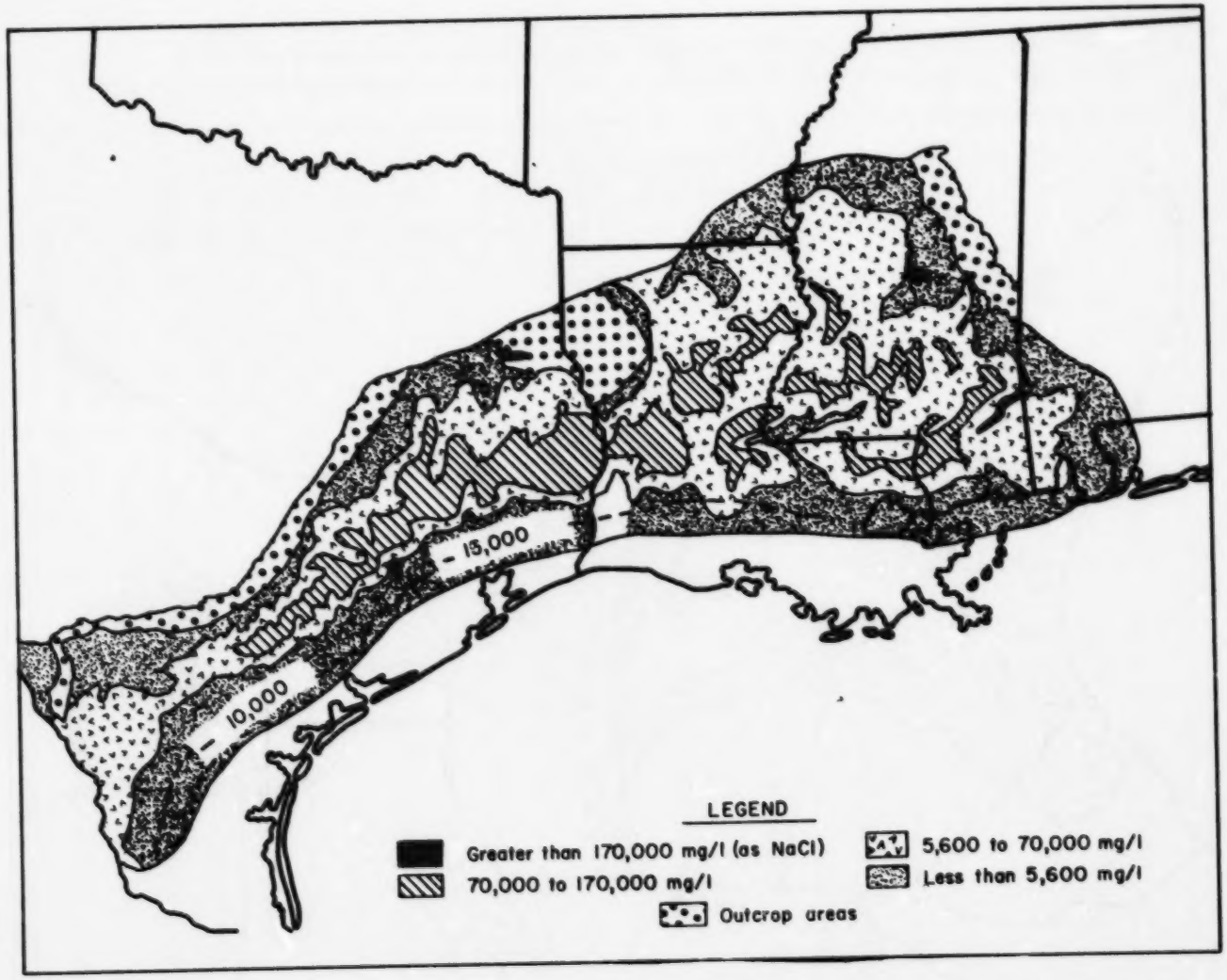


Figure 11. Salinity variations in formation waters at the base of the Lower Wilcox Formation located in portions of Texas, Louisiana, Arkansas, Mississippi, and Alabama.

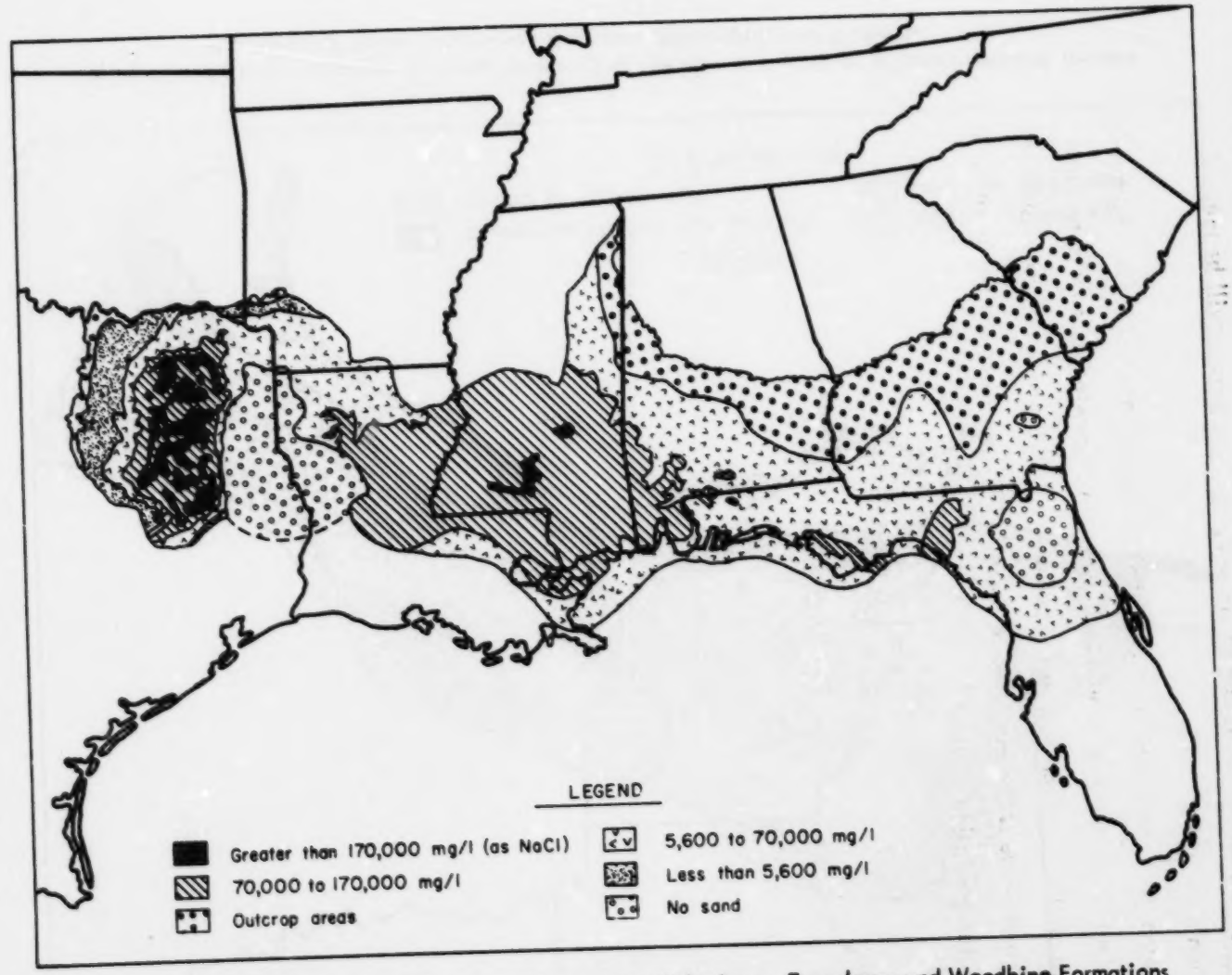


Figure 12. Salinity variations in formation waters of the Lower Tuscaloosa and Woodbine Formations located in portions of Oklahoma, Texas, Arkansas, Louisiana, Mississippi, Georgia, South Carolina, North Carolina, and Florida.

type, etc., of saline waters can be mapped, and in map form will be useful in pollution research.

Maps of certain ions in saline waters should be constructed for all areas of the United States and they should be drawn with a knowledge of the subsurface pressure gradients. Such maps are important in studying areas where subsurface injection of waste is contemplated or occurring. These maps can be drawn using a computer-controlled plotter.

SECTION VIII

POLLUTION OF FRESHWATER AND LAND BY BRINES

Waters associated with petroleum in subsurface formations usually contain many dissolved ions. Those dissolved ions most commonly present in greater than trace amounts are sodium, calcium, magnesium, potassium, barium, strontium, ferrous iron, ferric iron, chloride, sulfate, sulfide, bromide, and bicarbonate. Dissolved gases in these waters often include carbon dioxide, hydrogen sulfide, and methane. The stability of petroleum-associated brine is related to the constituents dissolved in it, the chemical composition of the surrounding rocks and minerals, the temperature, the pressure, and the composition of any gases in contact with the brine. A recent case study of a fresh water aquifer that was polluted by oilfield brine indicated that the aquifer would remain polluted for more than 250 years.[10]

Scale inhibitors are added to waters and brines to prevent the precipitation reactions. Some of the chemicals used in these inhibitors are listed in Table 8.

Table 8. CHEMICALS USED IN SCALE INHIBITORS

Ethylenediamine tetraacetic acid salts
Nitrilotriacetic acid salts
Sodium hexametaphosphate
Sodium tripolyphosphate
Sodium carboxymethyl cellulose
Aminotrimethylene phosphate

Knowledge of the oxidation state of dissolved iron in brines is important in compatibility studies. Brines in contact with the air will dissolve oxygen, and their oxidation-reduction potential (Eh) generally will be from 0.35 to 0.50 mv. Brines in contact with petroleum in the formation normally will have an Eh lower than 0.35 mv, as will waters in contact with reducible hydrocarbons. Any change in the oxidation state of brine containing dissolved iron may result in the deposition of dissolved iron compounds.

The sediments or precipitate formed from brines can cause environmental pollution directly or indirectly. For example, if the produced brines are stored in a pond, the sediments may cause soil pollution; if the brines are injected into a disposal well, the sediments may plug the face of the disposal formation, resulting in the necessity to increase injection pressures, which may rupture the input system.

The amount of saltwater or brine produced from oil wells varies considerably with different wells and is dependent upon the producing formation and the location, construction, and age of the well. Some oil wells produce little or no brine when first produced, but as they are produced, they gradually produce more and more brine. As some wells become older, the produced fluids may be more than 99 percent brine; or for each cubic meter of oil coming to the surface, 100 cubic meters or more of brine also is produced. The produced brines differ in concentration, but usually consist primarily of sodium chloride in concentrations ranging from 5,000 to more than 200,000 ppm; the average probably is about 40,000 ppm. For comparison, note that seawater contains about 20,000 ppm of chlorides. One cubic meter of brine containing 100,000 ppm of chloride will raise the chloride content of 400 cubic meters of fresh water above the maximum recommended for drinking water, which is 250 ppm of chloride. Petroleum-associated brines may escape and contact freshwater or soil in different ways. For example, to protect the upper freshwaters from the deeper mineralized waters that might rise in the drilled well, the upper portion of the well is sealed by a string of cemented surface casing. If

a well has insufficient surface casing, an avenue may be provided for the escape of brines if they are under sufficient hydrostatic head to cause them to rise in the hole to the surface or to the level of freshwater sands.

Handling the tremendous volume of brine produced simultaneously with petroleum is hazardous. Basically, the problem is to handle and dispose of the brine in such a manner that it does not contact soil or freshwater and cause detrimental pollution.

Currently, some produced brines are being discharged into approved surface ponds, whereas most brines are returned underground for disposal or to repressure secondary oil or gas recovery wells. The discharge of brines to any surface drainage is strictly prohibited in most states. Potential water and soil pollution problems are associated with both disposal methods. For example, if the surface pond is faulty, the brine will contact the soil and various chemical reactions will occur between the soil and the brine. Sometimes the brine will pass through the soil, reappear at the surface, and produce scar areas, and sometimes it will pollute the soil; leaching will pollute surface streams or shallow surface aquifiers.

RESIDUAL SALT CONCENTRATIONS BENEATH OR NEAR ABANDONED UNSEALED DISPOSAL PONDS

Unsealed surface ponds used for the disposal of oilfield brines have polluted fresh surface waters, potable groundwaters, and fertile land. Because of chemical and physical phenomena and dispersion, the movement of soluble pollutants from these ponds is complex. For example, the soluble pollutants move slowly in relation to the soil water flow rate, and dispersion effects a displacement that causes the contaminated zone to grow.

The Kansas State Department of Health studied the soils beneath and near an old unsealed brine disposal pond that had been abandoned for 10 years. During its use, the pond received more than 29,000 metric tons of salts, and most of those soluble salts probably escaped by soil leaching and down-drainage and penetrated

below the underlying limestone formation. Eleven test holes were drilled into the soil and shale beneath and adjacent to the pond, both above and below the natural drainage slope. Chemical analysis of the test hole core samples indicated that more than 430 tons (about 1.4 percent of the original) of the soluble residual salt still remained to be leached out of the soil and shale in the pond area. This amount of soluble or leachable salt remaining in the area indicates that the return of the subsurface water and soil to their prepollution level is a very slow process and may take several decades. Network pollution zones appear to form where formation fracture conjugates occur. Leaching appears to be entirely dependent upon the flushing mechanism provided by meteoric water.

The cation concentrations in the clay minerals in the soils near the disposal pond were evaluated by x-ray diffraction techniques to trace cation transportation rates. Chloride analysis was selected as the most useful single means of detecting the presence of oilfield brine pollution, but the associated cation concentration should also be determined to formulate a more complete picture. Cation adsorption studies are apparently useful in differentiating brine-polluted soil and shale; clay mineral studies provide the information on the environmental characteristics of the pollution media; and cation exchange information aids in explaining the apparent differential transportation rates of ions in brine seepage solutions.[11]

SUBSURFACE DISPOSAL

A problem associated with subsurface brine disposal is casing leaks in the disposal well, which could allow the brine to enter freshwater aquifers. Figure 13 shows how an improperly designed disposal well and a leaky oil well can pollute a freshwater aquifer. Erroneous geologic knowledge of the subsurface formation into which the brine is being pumped presents another problem. Brine usually is pumped into a subsurface formation that contains similar brine; however, exact knowledge of the faulting and fracturing of such a subsurface formation is difficult to determine. Because the brine is pumped into the formation, bottomhole pressure

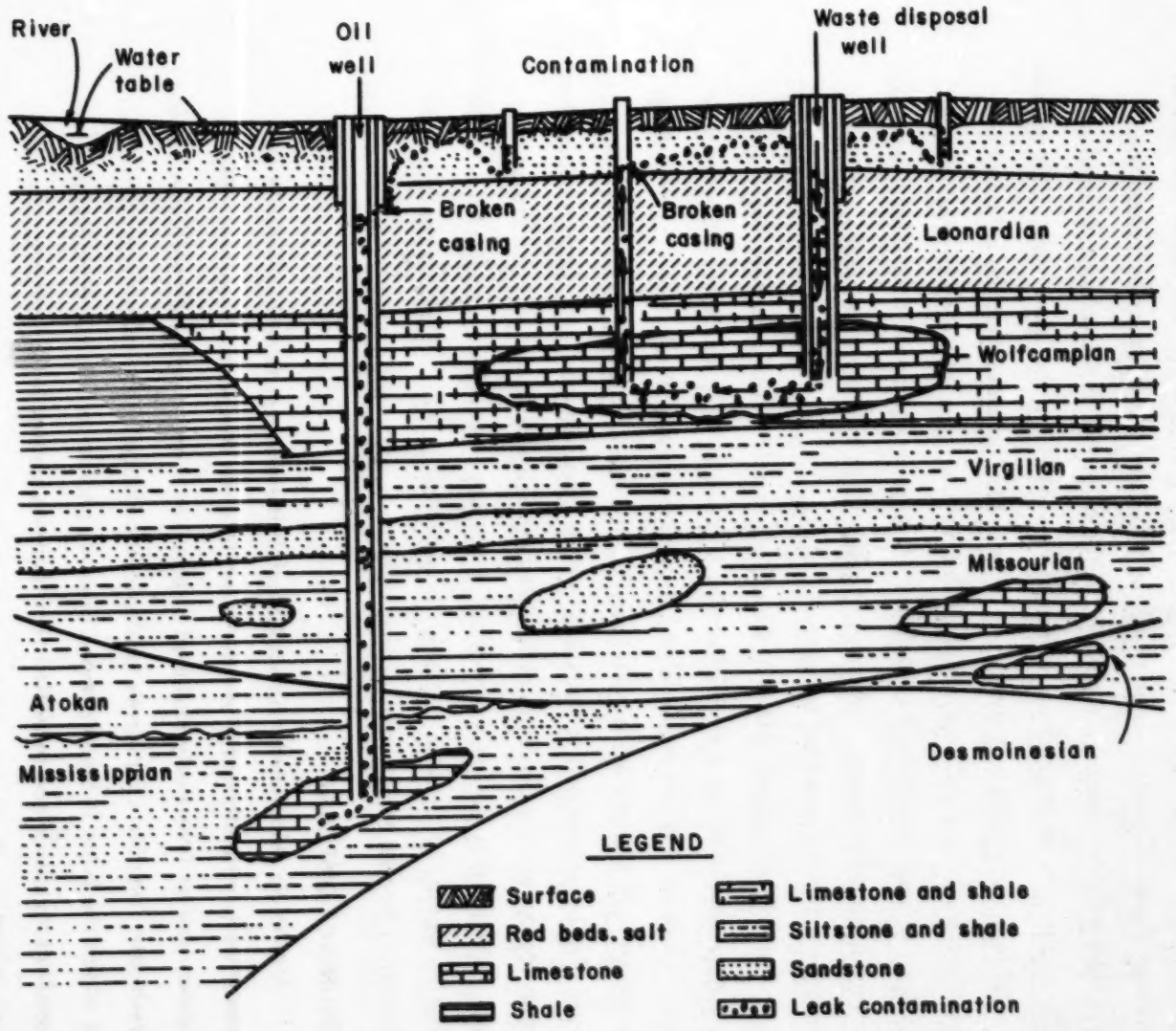


Figure 13. Routes by which salt water can enter freshwater wells from faulty oil or disposal wells.

must not exceed 0.23 kg/cm^2/m of overburden, or the hydraulic pressure may cause fracturing and in time, the wastes may migrate to a freshwater zone.

Petroleum-associated brines from two different formations may form precipitates if they are mixed. For example, with a well used for disposal of brines produced from several producing oil wells, it is imperative that precautions be taken in mixing and treating the brines before injection. If the brines are incompatible and inappropriate precautions are taken, there is a possibility that deposits will form and filter out on the face of the injection formation, thus reducing the permeability. The quantity of deposits formed from incompatible brines depends on ions present. The more common deposits resulting from reactions of incompatible brines are gypsum ($CaSO_4 \cdot 2\ H_2O$), anhydrite ($CaSO_4$), aragonite ($CaCO_3$), calcite ($CaCO_3$), celestite ($SrSO_4$), barite ($BaSO_4$), triolite (FeS), and siderite ($FeCO_3$).

Subsurface brine disposal can be categorized as confinement or containment; confinement is the placement of brines in a horizon where any movement can be controlled or monitored, while containment is the placement that precludes the movement of the brines out of a formation or zone. Containment cannot be used for an unlimited supply of brine, but confinement necessitates the monitoring of the migration of the brines. The necessary knowledge to define the hydrodynamics of brines injected into subsurface environments is expensive to obtain, and much of the necessary fundamental knowledge of subsurface formations is not available. Formations into which brines are often pumped for disposal are called salaquifers, and these zones consist of permeable sedimentary rock. Some information needed before such a zone can be used for disposal operations is as follows: 1) How big is the zone? 2) If the brine migrates in the zone, might it reappear in another zone or perhaps migrate to the surface? 3) What mechanisms control movement in a given salaquifer or perhaps out of it? 4) What steps are necessary to assure containment or confinement of the brine within the salaquifer? It is difficult, if not

impossible, to develop adequate prior knowledge concerning how or where escape channels may occur from a salaquifer. Test drilling is the only known method that can provide such knowledge, and such drilling is expensive, as is the subsequent evaluation.

SECTION IX

USE OF SALINE WATERS FOR DESALINATION TO PRODUCE FRESHWATER AND VALUABLE MINERALS

Dwindling freshwater supplies and polluted supplies have increased research on how to best obtain freshwater from saline water. Several plants throughout the world produce freshwater from seawater. The price of water for municipal purposes is a highly specific thing. The availability of freshwater and costs of obtaining it vary from place to place. Conventional water supplies range in cost from a few dollars per thousand cubic meters to over $260 per thousand cubic meters.

The average cost of conventional water supplies in the United States was $100 per thousand cubic meters in 1952. This was chosen as the goal for saline water conversion costs. Several authors have estimated ultimate costs of saline water conversion based on thermodynamic considerations. Dodge and Eshaya [12] have examined the minimum expected costs for saline water conversion. Prior to their calculations, other authors reported seawater conversion costs to be ultimately less than $79 per thousand cubic meters. Dodge and Eshaya[12] expanded earlier work to look at departure from isothermal operation, finite product recovery, differential as opposed to single-stage operation, and salt concentration in the feed. They found that $90 per thousand cubic meters is the smallest cost for desalination of seawater that contains about 31,300 ppm of sodium chloride.

Consider the case for converting brackish water with 5,000 ppm sodium chloride. For converting 50 percent of the feed to freshwater, 187 kW-hr per 1,000 cubic meters was the power requirement. To convert seawater with 35,000 ppm of dissolved solids conversion, the power requirement was 1,530 kW-hr per 1,000 cubic meters. Both calculations were for 50 percent recovery of freshwater from feed, where the average power costs used in determining conversion costs are 1.5 cents per kW-hr. At this rate, the difference in power costs for seawater over brackish water is $20 per 1,000 cubic meters.

Oilfield brines contain up to seven times the concentrations of dissolved salts compared with seawater. Would the power be seven times again as expensive per 1,000 cubic meters? At over $132 for power and $92 for other costs, the cost of obtaining freshwater from oilfield brines probably would be prohibitive when consideration is given to the other sources for feed to a conversion plant in the same area. An additional factor is that most oilfield brines with their high concentrations are nearly saturated. Removing 50 percent of the water would in essence leave a precipitated salt. Therefore, since no conversion processes under study deal with saturated brine effluents, it is not technologically feasible to completely desalt oilfield brines at this time.

RECOVERY OF VALUABLE MINERALS FROM SALINE WATERS

The "brine refinery" concept would require a process plant the size of a large petroleum refinery.[13] The market prices used in the concept were for the recovery and sale of the pure elements. The $3 billion in sales from 0.95 billion cubic meters of brine is the highest sales income possible that would result from recovering and selling the minerals in the form that gives the highest unit price.

Consider a "brine refinery" system that would gather 22 million cubic meters of brine per year. The cost of gathering and disposing of this brine would be approximately 9.4 cents per cubic meter. The question is whether or not minerals could be sold at a profit such that the disposal expense would be negated or a profit made. First, the minerals to be sold must be determined. At 7 ppm lithium, 163 metric tons per year could be produced. This is a large fraction of present consumption and probably would depress the sale price. The same holds true for most other elements of such a refinery.

The assumptions lead to a brine refinery system that would process 22 million cubic meters of brine per year and would yield minerals worth $35 million.

Assuming a 15-percent return on investment and a profit of 15 percent of sales, the plant would require $35 million investment and yield 23.6 cents per cubic meter of brine processed. The original disposal operation without mineral recovery was such that only $6 million was invested. The "brine refinery" would turn brine disposal into a profit. But the new investment is six times that for disposal only.

Would a chemical company be interested in such an operation since they operate at about a 15-percent return? Companies that currently remove minerals from brines use brines that are more concentrated in the minerals desired. It is doubtful that a process could combine several less economical operations into a more economical one, and this would probably be true even if the brine were supplied to a chemical company free of charge. Only in the special case where an oilfield brine contained a concentration of dissolved minerals very near a proven economic brine would the oilfield brine be a best alternate. Therefore, a tax incentive for pollution abatement or some other economic incentive such as price increase of recovered chemicals is probably necessary. Figure 14 illustrates a flowsheet for producing freshwater and valuable minerals from brines.

Table 9 illustrates the approximate amount of valuable chemicals a million kilograms of brine produced from a given depth should contain before it can be considered of economic value at present market conditions. The values shown in Table 9 should allow a profit if conventional or better recovery operations are utilized. The marketed end product will influence the selection of the recovery operation as well as the delivered price. The price information used to make the approximations was taken from the Bureau of Mines.[14]

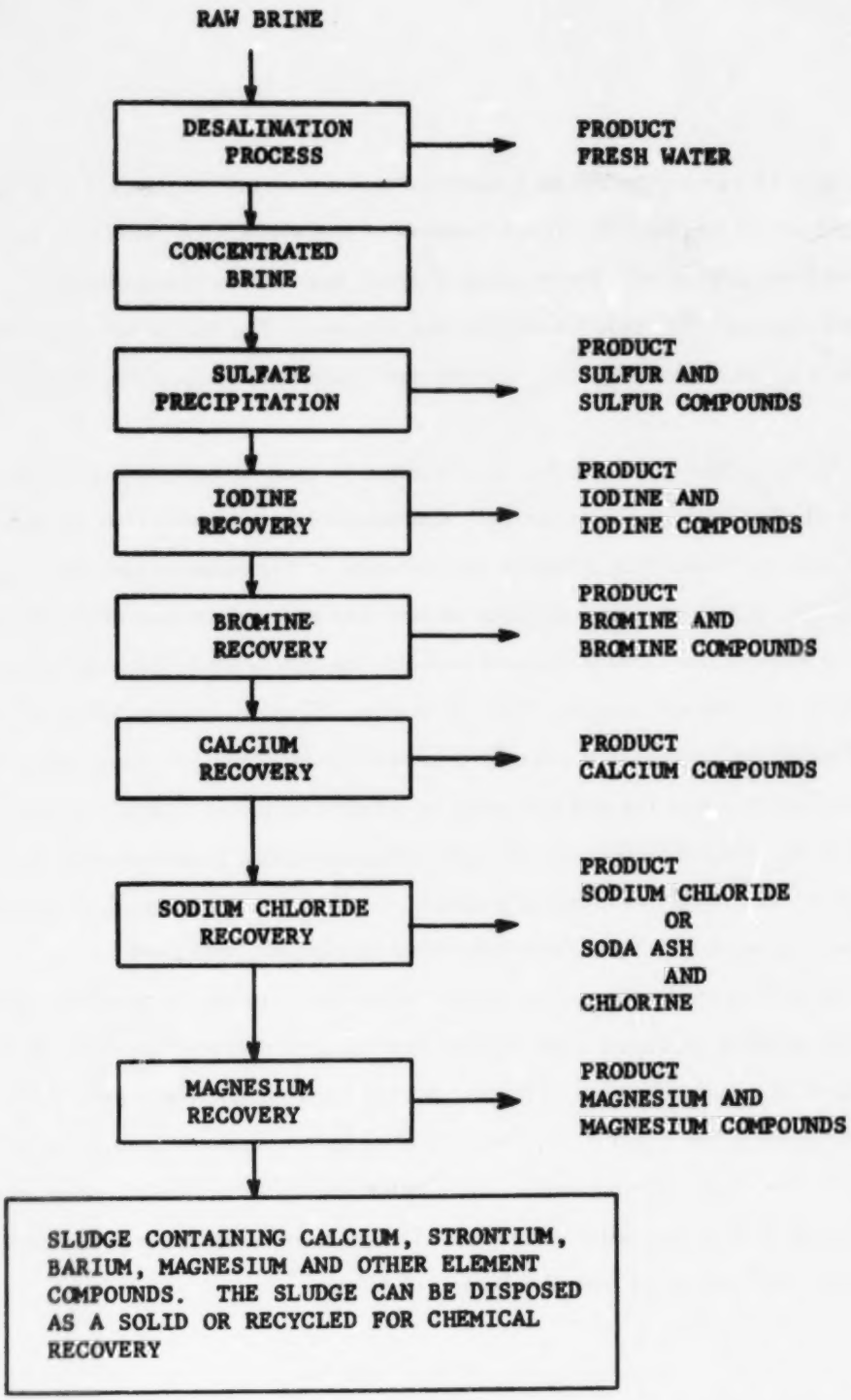

RAW BRINE
DESALINATION PROCESS
PRODUCT FRESH WATER
CONCENTRATED BRINE
SULFATE PRECIPITATION
PRODUCT SULFUR AND SULFUR COMPOUNDS
IODINE RECOVERY
PRODUCT IODINE AND IODINE COMPOUNDS
BROMINE RECOVERY
PRODUCT BROMINE AND BROMINE COMPOUNDS
CALCIUM RECOVERY
PRODUCT CALCIUM COMPOUNDS
SODIUM CHLORIDE RECOVERY
PRODUCT SODIUM CHLORIDE OR SODA ASH AND CHLORINE
MAGNESIUM RECOVERY
PRODUCT MAGNESIUM AND MAGNESIUM COMPOUNDS
SLUDGE CONTAINING CALCIUM, STRONTIUM, BARIUM, MAGNESIUM AND OTHER ELEMENT COMPOUNDS. THE SLUDGE CAN BE DISPOSED AS A SOLID OR RECYCLED FOR CHEMICAL RECOVERY

Figure 14. Diagramatic flowsheet for producing freshwater and valuable elements from brines.

Table 9. DOLLAR VALUE OF DISSOLVED CHEMICALS A BRINE SHOULD CONTAIN PER MILLION KILOGRAMS OF BRINE PRODUCED FROM A GIVEN DEPTH

Value of dissolved chemicals per million kilograms of brine for economic production	Depth of well, meters
$ 462	760
$ 968	2,130
$1,430	3,050

Factors that must be considered in evaluating a saline water as an economic ore are the cost of bringing it to the factory, the cost of the recovery process, and the cost of transporting the recovered products to market. Assuming that a brine is produced only for the purpose of recovering its dissolved chemicals, a prime factor is the cost of pumping the brine. It will cost less to produce the brine from a shallow well than from a deep well. Therefore, neglecting other factors, a brine must contain a certain amount of recoverable chemicals before it can be considered economically valuable, and the farther it must be pumped, the more chemicals it must contain.

Today the possibility of recovering elements from brines that are pumped to the surface is increasingly important because the brines present a pollution hazard if their disposal is improper. One cubic meter of brine containing 100,000 ppm of chloride is capable of polluting 400 cubic meters of freshwater so that it is unfit for human consumption.

Table 10 illustrates the value that chemicals recovered from brines have at the market; however, because the market fluctuates, these values are approximate. The column on the left indicates the elements that are found in petroleum-associated

brines, and the second column indicates the concentration that a given brine must contain before it can be used to produce a given amount of chemical. For example, a brine containing 50,000 ppm of sodium will contain sufficient sodium in a million kilograms of brine to produce sodium chloride worth about $550.

Table 10. AMOUNT OF ELEMENT NECESSARY IN A MILLION KILOGRAMS OF BRINE TO PRODUCE A CHEMICAL WORTH $550 AT THE MARKET

Element in the brine	Concentration of element in a million kilograms of brine, parts per million	Market product
Sodium	50,000	Sodium chloride
Potassium	14,000	Potassium chloride
Lithium	170	Lithium chloride
Magnesium	8,000	Magnesium chloride
Calcium	11,000	Calcium chloride
Strontium	4,000	Strontium chloride
Boron	1,400	Sodium borate
Bromine	1,700	Bromine
Iodine	250	Iodine
Sulfur	5,300	Sodium sulfate

The data in Table 10 indicate that some petroleum-associated waters contain sufficient sodium to establish them as economic for the production of sodium chloride. This is not necessarily true, because factors such as market demand, ease of recovery, and proximity to market may be discouraging in certain geographic areas. Such factors must be fully considered before startup of a chemical from brine recovery

operation. One important goal that should not be discounted or overlooked is developing a means of ultimately disposing of these brines to eliminate any pollution hazard. Coupling of this goal with the fact that many of these brines contain economic concentrations of several elements should make such recovery operations more attractive. Additionally, several important chemicals can be produced from these elements instead of those shown in the market product column in Table 10. An example is soda ash, which is a basic chemical in many manufacturing processes. Furthermore, the figures shown in Table 9 are applicable only if the brine is produced solely for the recovery of its dissolved chemicals. If the brines are pooled from several petroleum production operations, the cost of pumping the brine becomes less, and the necessary amounts of chemicals dissolved in a million pounds of brine become less.

Mixed Salts

Mixed salts are precipitated by evaporation of seawater and brines to produce crude salt separations. The costs of these separations are low compared to those of highly purified compounds or metals. There are several drawbacks that prevent greater use of this type of recovery. The product does not command a high price, the plant must be at the brine source, there must be solar evaporation conditions, and a local market must exist for the majority of the mixed salts. Uses that have been suggested include heattreating salt baths in the steel industry, raw materials for refractory or catalyst manufacture, and fertilizer components.

Precipitation other than by solar evaporation is accomplished by cooling or adding chemical agents. Simple cooling may be all that is necessary for more concentrated brines, but fractional crystallization is necessary for dilute brines such as seawater. Again, local markets dictate whether cooling or freezing processes will yield the correct products for a particular area. Adding chemicals to precipitate a specific product is the most fruitful of the nonsolar evaporation processes. Most of the processes have been aimed at the production of fertilizer.

Potassium and magnesium are the minerals in seawater that are most valuable for use in producing fertilizers. Salutsky and Dunseth[15] report that metal ammonium phosphates (MAP) containing magnesium, calcium, iron, manganese, copper, and many other trace metals comprise high-analysis fertilizer.

W. R. Grace Company started U.S. production of MAP fertilizer on a semicommercial scale in 1960 through the use of their patent issued in 1962.[16] The fertilizers are nonburning, long-lasting sources of nitrogen, phosphorus, and various trace metals. Because of their low solubility, MAP's will not cause salt injury to seeds or plants.

In magnesium ammonium phosphate, practically all of the P_2O_5 is available, and the size of the MAP granules applied to plants determines how long the nutrients will be available. Thus, availability of nutrients can be controlled by granulation and, since growing time varies from crop to crop, MAP's can be tailored to a specific crop. Therefore, fewer applications are necessary with MAP's than with fertilizers of higher solubility and high nitrification rates.

The W. R. Grace Co. developed the MAP process for two purposes. First, it is useful to remove scale-forming materials from seawater before desalination. Secondly, it would yield the valuable, high-analysis fertilizer, magnesium ammonium phosphate. In 1962, W. R. Grace Co. reported that the process was ready for the pilot plant.[16] The process is based on phosphate precipitation. To descale seawater and produce high-analysis fertilizer at the same time, wet-process phosphoric acid and anhydrous ammonia are added continuously to raw seawater. This precipitates the scale-forming elements--calcium, magnesium, iron, and other metals--as metal ammonium phosphates and other phosphates. The precipitated solids (MAP's) are removed by settling, and the descaled seawater is pumped to the saline water conversion plant. The descaled water holds only 1 percent of the original magnesium and 5 percent of the original calcium, thus representing a more optimum water for desalination. The slurry of MAP's is dewatered to about 35 to 40 percent solids by continuous centrifuges and then it is heated to 90° C. This

converts MAP hexahydrate to monohydrate. The slurry is filtered, washed, mixed with recycle fines, and granulated. Figure 15 shows a process flowsheet for producing descaled oilfield brine and fertilizer.

Several questions surround the economics of the process. For a plant descaling 3,800 cubic meters of seawater per day (output about 10,000 metric tons per year of fertilizer), the fertilizer would have to command a price higher than that of conventional farm fertilizers. The estimate assumes 1962 market prices for raw materials (phosphoric acid and ammonia) and does not take credit for the increased value of the descaled seawater. Because of its premium quality, MAP can go to the market as a speciality product.

In the phosphoric acid-ammonia process, 2 moles of ammonia per mole of MAP are lost to ammonium chloride in neutralizing the phosphoric acid. Using disodium phosphate in place of the acid loses no ammonia, and using monosodium phosphate only loses 1 mole of ammonia. If a cheap method were developed for producing the sodium phosphates, ammonia waste would be reduced. The simplest method for producing sodium phosphates involves the neutralization of phosphoric acid with either dilute sodium hydroxide or soda ash. Caustic soda and chlorine can both be produced from sodium chloride brines.

At the present time, many petroleum-associated brines are injected into subsurface strata, and it is assumed that they are thus disposed of permanently.[17] However, this method of disposal appears subject to question, because in some instances, freshwaters apparently have been polluted by disposal of brines. Subsurface disposal operations are suspected in certain areas as possibly contributing to increased earthquakes and ground tremors.[18, 19]

The storage of brines in earthen pits is known to cause pollution of nearby soils and streams. Such ponds that have been abandoned for 10 years still contribute to soil pollution.[11] Sound conservation should favor the recovery of

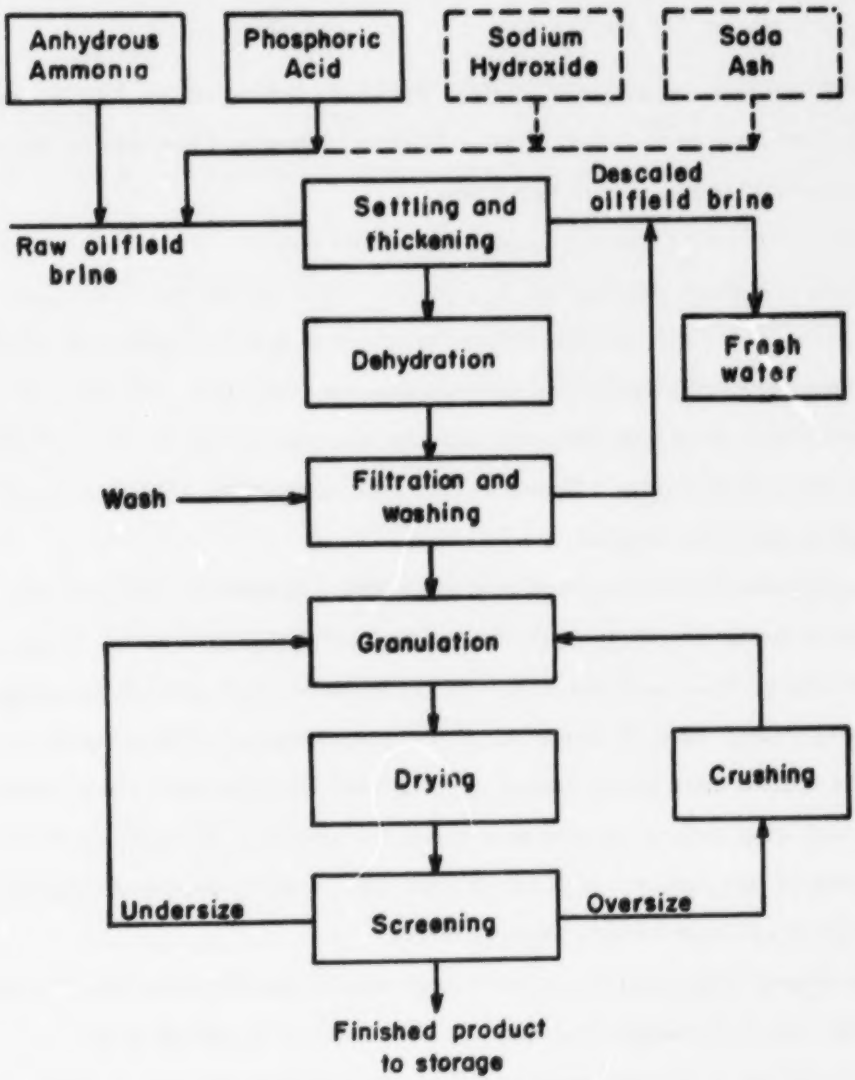


Figure 15. Diagramatic flowsheet for producing descaled seawater and fertilizer.

valuable elements from brines, and with proper planning, the recovery processes should aid in the ultimate disposal of unwanted brines. Conservation of this type not only will develop new resources, but will benefit the oil producer and the national economy and will aid in abating pollution of soils, potable waters, and streams.

WORK NECESSARY FOR AN EXACT PRELIMINARY EVALUATION

Aries[20] spells out the marketing research techniques employed in the chemical industry. There are ways to determine quickly where a market for a product is. Usually these places are currently served by some producer or another. If the competition is located far from the market, then an evaluation of a closer area source is readily made. To find product users, the following methods and approaches are utilized: advertising, company analysis, product analysis, industry analysis, use analysis, and other miscellaneous methods. If new markets must be found, the following types of work are utilized: personal interview, questionnaire, trade analysis, company records, and published sources. Before an economic analysis can be made for a given area, probably several man-months of the above-listed methods would be required. The product of this type of market study would be a list of elements and compounds that could be sold from a given place. The quantities and prices obtained would then allow an economic calculation of the production costs.

With the quantities, prices, and production costs in hand, it is still not a simple matter to determine what type of plant to operate. Regardless of who the investor might be, he will want to know what return on investment he will get, what risk is involved, and what payout period exists for the project. Depending on the investor, he may want to limit the plant size by the amount of money he can invest. This does not simply scale down the plant. It may rearrange various

ratios of certain products produced in order to give the investor the combination of profits, return on investment, risk, and actual size of investment that he desires.

LOCATIONS OF VALUABLE BRINES

Figures 16, 17, 18, and 19 are maps showing areas in the United States where brines containing high concentrations of sodium, calcium, magnesium, and bromine, respectively, are found.

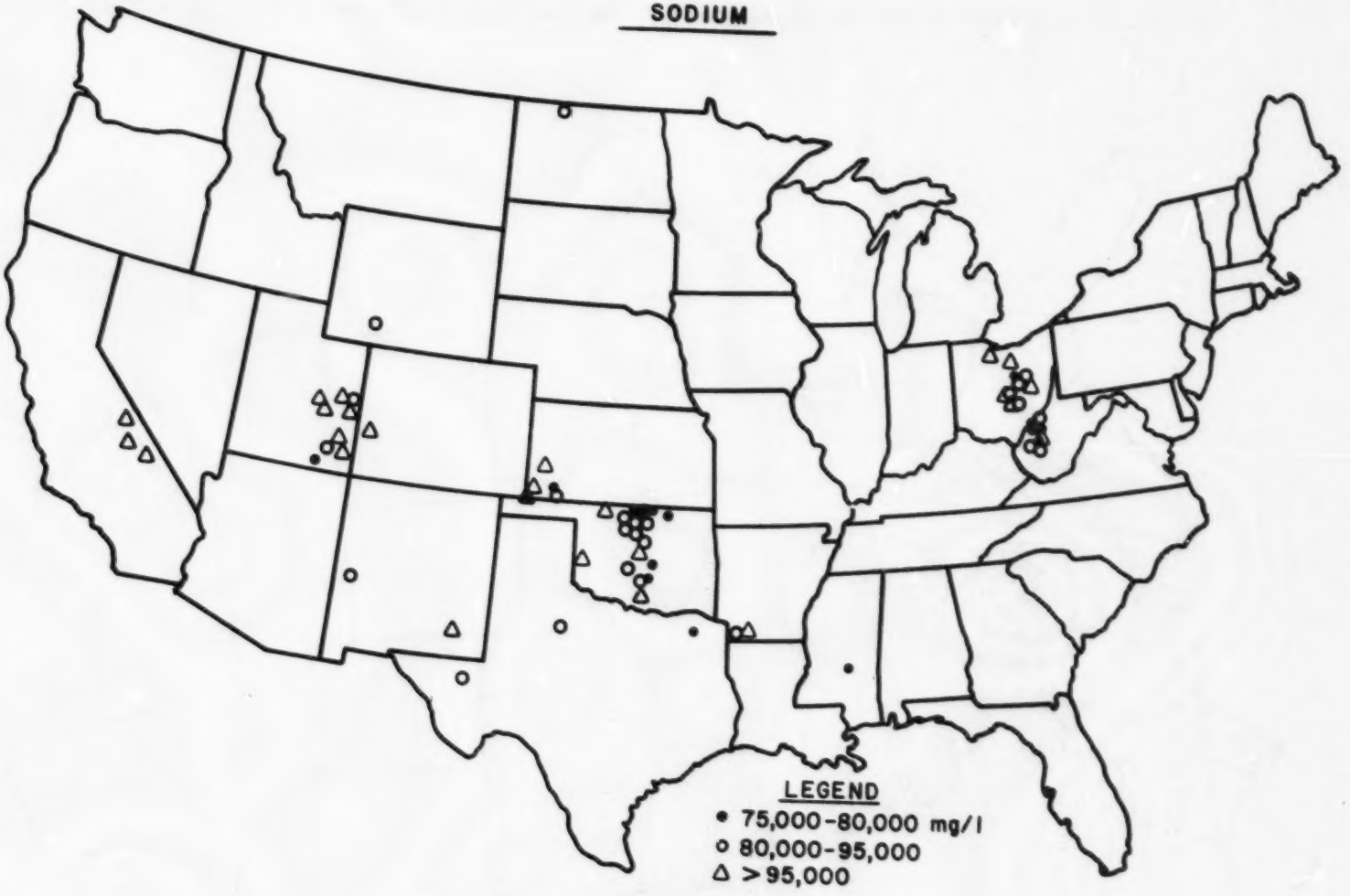


Figure 16. Approximate geographic locations of brines containing high concentrations of sodium.

Figure 17. Approximate geographic locations of brines containing high concentrations of calcium.

Figure 18. Approximate geographic locations of brines containing high concentrations of magnesium.

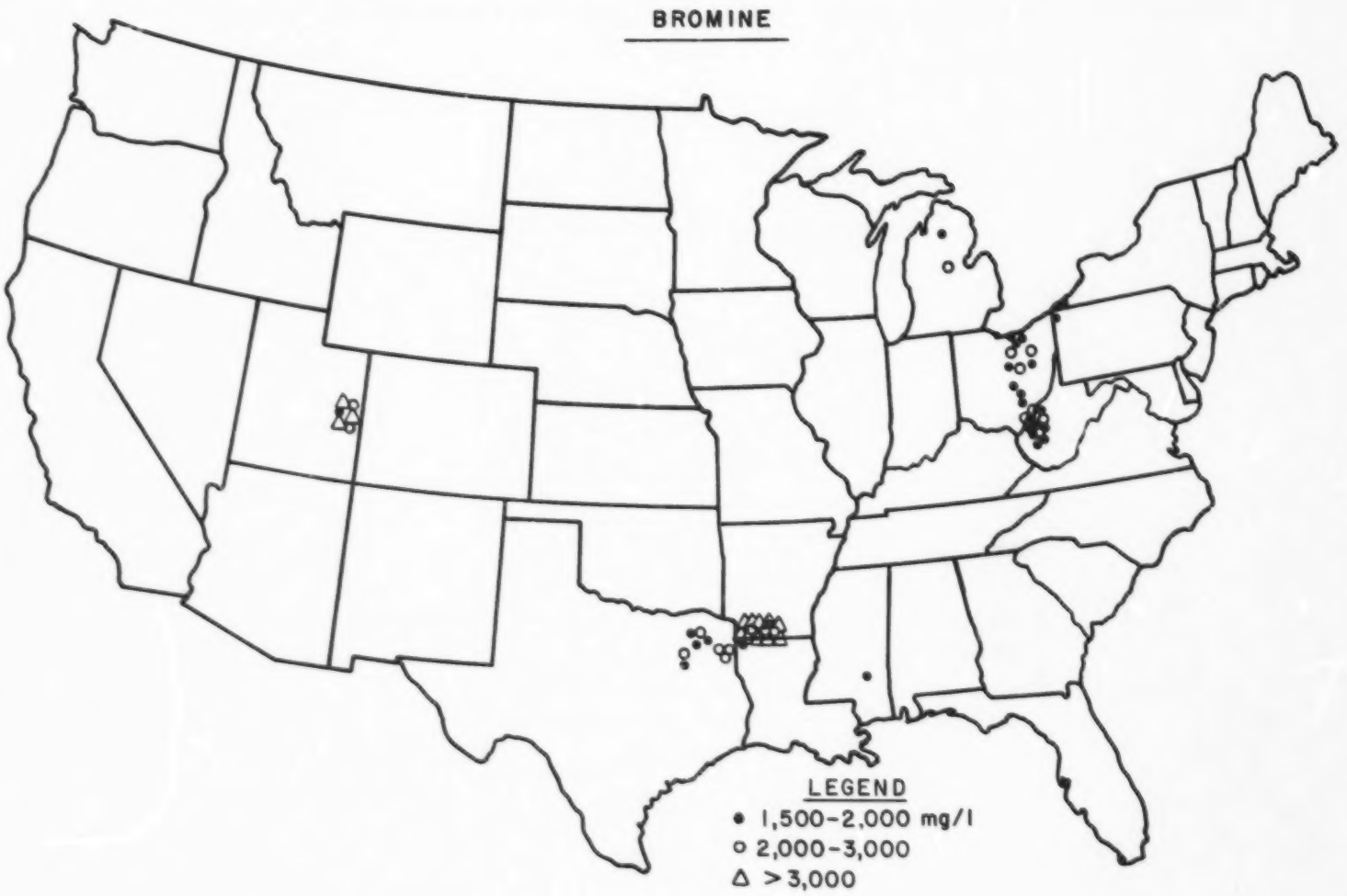


Figure 19. Approximate geographic locations of brines containing high concentrations of bromine.

SECTION X

REFERENCES

1. Piper, A. M. A Graphic Procedure in the Geochemical Interpretation of Water Analyses. U.S. Geol. Survey Ground Water Note 12, 14 pp. (1953).
2. Reistle, C. E. Identification of Oil-Field Waters by Chemical Analysis. U.S. BuMines Tech. Paper 404, 25 pp. (1927).
3. Stiff, H. A. The Interpretation of Chemical Water Analysis by Means of Patterns. J. Petrol. Tech., 3, pp. 15-17 (1950).
4. Tickell, F. G. A Method for Graphical Interpretation of Water Analysis. Calif. State Oil and Gas Supervisor, 6, pp. 5-11 (1921).
5. Morgan, C. E., R. J. Dingman, and J. M. McNellis. Digital Computer Methods for Water-Quality Data. Ground Water, 4, pp. 35-42 (1966).
6. Morgan, C. O., and J. M. McNellis. Stiff Diagrams of Water-Quality Data Programmed for the Digital Computer. Kans. State Geol. Survey. Special Distribution Pub. 43, 27 pp. (1969).
7. Angino, E. E., and C. O. Morgan. Application of Pattern Analysis to the Classification of Oil-Field Brines. Kans. State Geol. Survey. Computer Contribution 7, pp. 53-56 (1966).
8. Collins, A. G. Geochemical Classification of Formation Waters for Use in Hydrocarbon Exploration and Production. M.S. Thesis. University of Tulsa, Tulsa, Okla., 63 pp. (1972). Also Chapter 8 of Book, Geochemistry of Oilfield Waters, Authored by Collins, Elsevier Publishing Company, In Press.
9. Visher, G. S. 1961 Unpublished Report, Sinclair Oil Company, Now at the University of Tulsa, Tulsa, Okla.
10. Fryberger, J. S. Rehabilitation of a Brine-Polluted Aquifer. Environmental Protection Agency Report, EPA-R2-72-014, 61 pp. (1972).

11. Bryson, W. R., G. W. Schmidt, and R. E. O'Connors. Residual Salt of Brine Affected Soil and Shale, Potwin Areas, Butler Co., Kansas. Kansas State Dept. of Health Bull. 3-1, 28 pp. (1966).

12. Dodge, B. F., and A. M. Eshaya. Thermodynamics of Some Desalting Processes. Advan. Chem. Ser., No. 27, American Chemical Society, Washington, D. C., 246 pp. (1960).

13. Collins. A. G. Here's How Producers Can Turn Brine Disposal Into Profit. Oil and Gas J., 64, pp. 112-113 (1966).

14. Bureau of Mines. Metals, Minerals, and Fuels. Minerals Yearbook. Vol. I-II, 1208 pp. (1968).

15. Salutsky, M. L., and M. G. Dunseth. Recovery of Minerals from Sea Water by Phosphate Precipitation. Advan. Chem. Ser., No. 38, American Chemical Society, Washington, D.C. 199 pp. (1962).

16. Anonymous. Descaling: Route to MAP. Chem. Eng. News, 40, pp. 52-53 (1962).

17. Crouch, R. L. Investigation of Alleged Ground-Water Contamination, Tri-Rue and Ride Oil Fields, Scurry County, Texas. Texas Water Commission Rept. LD-0464-MR, 16 pp. (1964).

18. Evans, D. M. The Denver Area Earthquakes and the Rocky Mountain Arsenal Disposal Well. The Mountain Geologist, 3, pp. 23-26 (1966).

19. Bardwell, G. E. Some Statistical Features of the Relationship Between Rocky Mountain Arsenal Waste Disposal and Frequency of Earthquakes. The Mountain Geologist, 3, pp. 37-42 (1966).

20. Aries, R. S. Marketing Research in the Chemical Industry. Chemonomics, New York, N. Y., 220 pp. (1954).

USER INFORMATION & STATION DATA
(FWPCA Storet System)

U.S. DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

AGENCY CARD

AGENCY (USER) CODE	(BLANK)	UNLOCKING KEY
2 1 0 K 1 1 R S		9 9 9 9 9 9 9 9
1 — 8	9 — 16	17 — 24

USER NAME, LOCATION, PROJECT, ETC.
U S B M A G C O L L I N
25 — 42

USER NAME, LOCATION, PROJECT, ETC. (Cont.)	FEET OR METERS	STORE CODE
S 9 1 8 5 8 4 2 2 8 2	F	
43 — 62	63	64 — 65

(F) - FEET
(M) - METERS

STATION TYPE	UNLOCKING DATE		CONTROL CODE	
	YEAR	MO.		
0 2 4 1 1 2 1 0	9 9	9 9		A
66 — 73	74 — 75	76 — 77	78 — 79	80

STATION CARD

SEQUENCE NUMBER	PRIME STATION CODE (Left Justify)	(BLANK)
	4 8 0 0 2 6	
1 — 3	4 — 18	19 — 33

(1) SECONDARY STATION CODE (Left Justify)	(2) SECONDARY STATION CODE (Left Justify)
34 — 45	46 — 57

(3) SECONDARY STATION CODE (Left Justify)	FWPCA ASSIGNED CODES			CONTROL CODE	
	STATE	COUNTY	CITY		
	4 8	2 7 0		N S	S
58 — 67	68 — 69	70 — 72	73 — 77	78 — 79	80

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

STORET II - LOCATION DATA

HEADER CARD I *(Required)*

CARD SORTING NUMBER _____ [ ][ ][ ] 1-3
4-6 BLANK

LATITUDE *(Degrees, Minutes, 0.1 Seconds)* _____ [2][7][3][0][0][7][9] 7-13

LONGITUDE *(Degrees, Minutes, 0.1 Seconds)* _____ [0][9][8][0][1][2][1][4] 14-21

AGENCY CODE _____ [ ][ ][ ][ ][ ][ ] 22-27

PRECISION CODE *(Use for original storage only)* _____ [1] 28

UNITS CODE FOR DEPTH *(F for Feet and M for Meters)* _____ [F] 29

TOTAL DEPTH OF WATER OR WELL *(Use for original storage only)* _____ [5][7][6] 30-32

STATE CODE *(Use for original storage only)* _____ [4][8] 33-34

TYPE OF STATION CODE *(Use for original storage only)* _____ [ ][ ][ ][ ][ ][ ][ ][ ] 35-42
43-67 BLANK

STATION CODE *(Optional, Left Justify)* _____ [ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ][ ] 68-79 [0] 80

HEADER CARD III *(Optional and Used for Original Storage Only)*

CARD SORTING NUMBER *(Same as Col. 1-3 on Card I)* _____ [ ][ ][ ] 1-3
4-12 BLANK

STATE NAME (13-28):
T E X A S

MAJOR BASIN NAME (29-52):
W E S T E R N G U L F (1 2)

MINOR BASIN NAME (53-79):
R I O G R A N D E L O W E R B E L O W P E C O S [3] 80

HEADER CARD IV *(Optional and Used for Original Storage Only)*

CARD SORTING NUMBER *(Same as Col. 1-3 on Cards I and III)* _____ [ ][ ][ ] 1-3
4-6 BLANK

MINOR BASIN NAME - CONT. FROM CARD III (7-19):
(1 0)

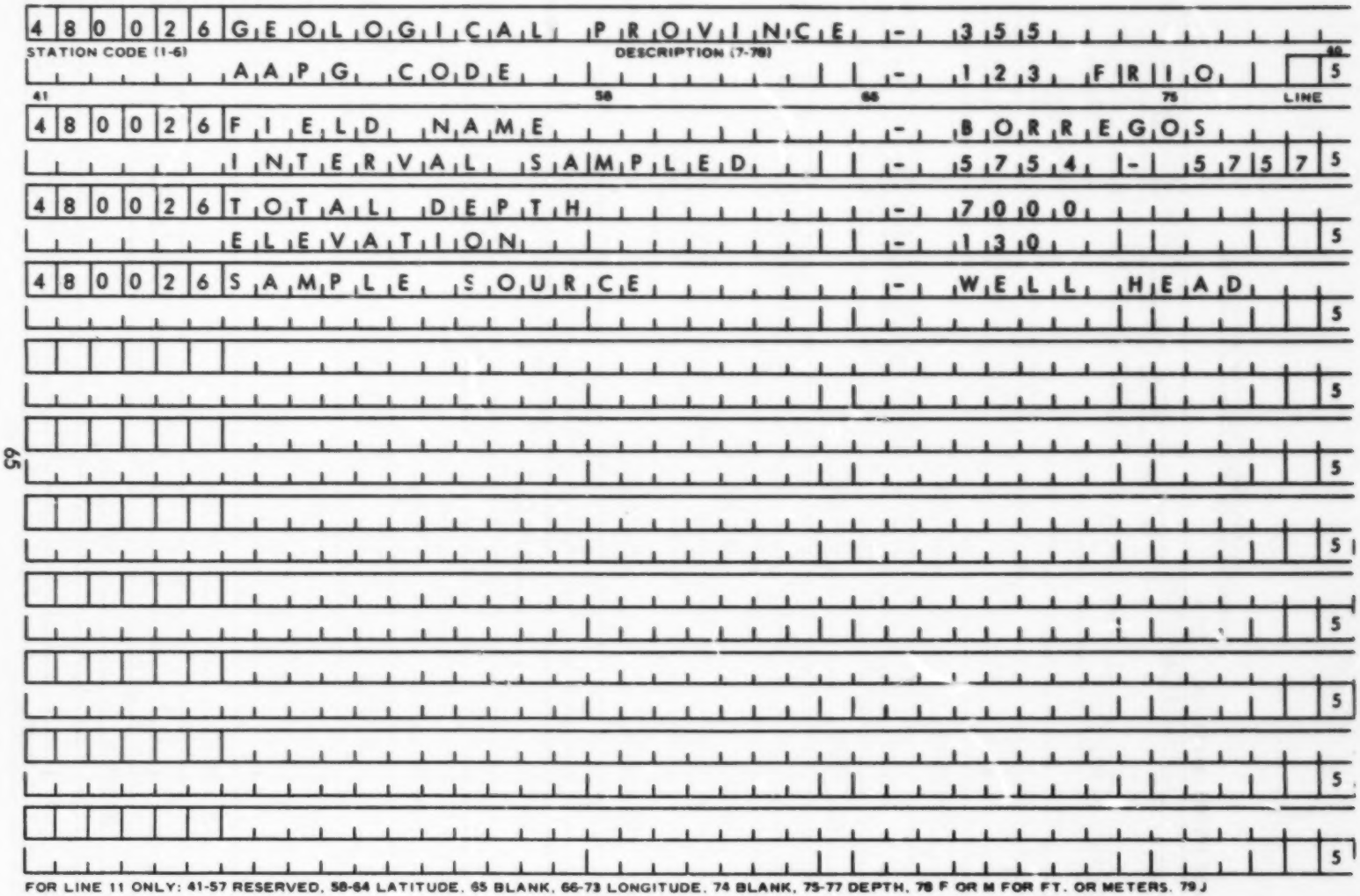
LOCATION NAME (20-51):
P R O D U C I N G W E L L

LOCATION NAME - CONT.:

52-79 BLANK [4] 80

DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

STORET I - LOCATION CARD V


4 8 0 0 2 6 GEOLOGICAL PROVINCE - 3 5 5
STATION CODE (1-6)
DESCRIPTION (7-79)
AAPG CODE - 1 2 3 FRIO
41
58
66
75
LINE
4 8 0 0 2 6 FIELD NAME - BORREGOS
INTERVAL SAMPLED - 5754 - 5757
4 8 0 0 2 6 TOTAL DEPTH - 7000
ELEVATION - 130
4 8 0 0 2 6 SAMPLE SOURCE - WELL HEAD

65

FOR LINE 11 ONLY: 41-57 RESERVED, 58-64 LATITUDE, 65 BLANK, 66-73 LONGITUDE, 74 BLANK, 75-77 DEPTH, 78 F OR M FOR FT. OR METERS, 79 J

FWPCA - 2d
2-66

U. S. DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

STORET SYSTEM - WATER QUALITY DATA

LABORATORY BENCH DATA	COMPUTER CODED DATA
STATION DESIGNATION; DATE OF SAMPLE YR. MO. DAY; HOUR & MINUTE OF SAMPLE OR LAST DATE OF COMPOSITE SAMPLE	STATION CODE SERIAL (1-6): 4 8 0 0 2 6; YR. MO. DAY (7-12): 6 3 1 1 0 7; (13-18)
ITEM pH UNIT Su	PARAMETER CODE (19-23): 0 0 4 0 0; VALUE (24-27): 6 6 0 0; EXPONENT (28): 1; (29): 1; RMKS (30)
ITEM Bicarbonate UNIT mg/l	0 0 4 4 0; 3 9 5 0; 1; 3; (31-39; 39-39; 40; 41; 42)
ITEM Total Solids UNIT mg/l	0 0 5 3 0; 3 0 3 4; 1; 5; (43-47; 48-51; 52; 53; 54)
ITEM Calcium UNIT mg/l	0 0 9 1 5; 7 3 5 0; 1; 3; (55-59; 60-63; 64; 65; 66)
ITEM Magnesium UNIT mg/l	COLUMN 80 (BLANK); CHG.; 0 0 9 2 5; 2 5 0 0; 1; 2; (67-71; 72-75; 76; 77; 78; 79)
ITEM Sodium UNIT mg/l	NEXT CARD - REPEAT COLUMNS 1-18 ABOVE; 0 0 9 3 0; 1 1 0 2; 1; 5; (19-23; 24-27; 28; 29; 30)
ITEM Chloride UNIT mg/l	0 0 9 4 0; 1 8 1 5; 1; 5; (31-39; 39-39; 40; 41; 42)
ITEM Sulfate UNIT mg/l	0 0 9 4 5; 1 1 0 0; 1; 2; (43-47; 48-51; 52; 53; 54)
ITEM Fe (total) UNIT µg/l	0 1 0 4 5; 2 3 0 0; 1; 2; (55-59; 60-63; 64; 65; 66)
ITEM Resistivity UNIT	COLUMN 80 (BLANK); CHG.; 7 2 0 1 0; 2 2 2 0; 0; 0; (67-71; 72-75; 76; 77; 78; 79)

FWPCA 2b (9-66) (Formerly PHS 4718-2)

U. S. DEPARTMENT OF THE INTERIOR
FEDERAL WATER POLLUTION CONTROL ADMINISTRATION

STORET SYSTEM - WATER QUALITY DATA

LABORATORY BENCH DATA		COMPUTER CODED DATA	
STATION DESIGNATION	DATE OF SAMPLE YR. MO. DAY	STATION CODE SERIAL (1-6)	YR. MO. DAY (7-12)
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HOUR & MINUTE OF SAMPLE OR LAST DATE OF COMPOSITE SAMPLE		(13-18)	
ITEM Resistivity Temperature UNIT °C		PARAMETER CODE (19-23)	VALUE (24-27) EXPONENT (28) RMKS (29) (30)
		7 2 0 1 4	2 2 7 0 1 2
ITEM Specific Gravity UNIT		7 2 0 1 3 (31-35)	1 0 2 1 (36-39) 1 1 (40 41) (42)
ITEM Specific Gravity Temperature UNIT °C		7 2 0 1 2 (43-47)	2 2 7 0 (48-51) 1 2 (52 53) (54)
ITEM UNIT		(55-59)	(60-63) (64 65 66)
ITEM UNIT		(67-71)	(72-76) (76 77 78) CHG. (79) COLUMN 80 (BLANK)
ITEM UNIT		NEXT CARD - REPEAT COLUMNS 1-18 ABOVE	
		(19-23)	(24-27) (28 29 30)
ITEM UNIT		(31-35)	(36-39) (40 41 42)
ITEM UNIT		(43-47)	(48-51) (52 53 54)
ITEM UNIT		(55-59)	(60-63) (64 65 66)
ITEM UNIT		(67-71)	(72-76) (76 77 78) CHG. (79) COLUMN 80 (BLANK)

PWPCA 2b (9-66) *(Formerly PHS 4718-2)*

SECTION XII

APPENDIX II

STORET DATE 72/02/15

480026
27 30 07.9 098 01 21.4 1
PRODUCING WELL
48 TEXAS
WESTERN GULF (12)
RIO GRANDE LOWER BELOW PECOS RIVER (10)
210K11RS 02412210
0999

PARAMETER				NUMBER	MEAN	VARIANCE	STAN DEV	MAXIMUM	MINIMUM	BEG DATE	END DATE
00400	PH		SU	1	6.60000			6.60000	6.60000	63/11/07	63/11/07
00440	HCO3 ION	HCO3	MG/L	1	395.000			395.000	395.000	63/11/07	63/11/07
00530	RESIDUE	TOT NFLT	MG/L	1	30340.0			30340.0	30340.0	63/11/07	63/11/07
00915	CALCIUM	CA,DISS	MG/L	1	735.000			735.000	735.000	63/11/07	63/11/07
00925	MGNSIUM	MG,DISS	MG/L	1	25.0000			25.0000	25.0000	63/11/07	63/11/07
00930	SODIUM	NA,DISS	MG/L	1	11020.0			11020.0	11020.0	63/11/07	63/11/07
00940	CHLORIDE	CL	MG/L	1	18150.0			18150.0	18150.0	63/11/07	63/11/07
00945	SULFATE	SO4	MG/L	1	11.0000			11.0000	11.0000	63/11/07	63/11/07
01045	IRON	TOTAL	UG/L	1	23.0000			23.0000	23.0000	63/11/07	63/11/07
72010	RESISTIV		BM	1	.222000			.222000	.222000	63/11/07	63/11/07
72012	SP GR	TEMP	CELSIUS	1	22.7000			22.7000	22.7000	63/11/07	63/11/07
72013	SPECIFIC	GRAVITY	BM	1	1.02100			1.02100	1.02100	63/11/07	63/11/07
72014	RESISTIV	TEMP	CELSIUS	1	22.7000			22.7000	22.7000	63/11/07	63/11/07